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An Intersystem Transition in the First Spectrum of Beryllium

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The intersystem line from the transition $2s^2\ {}^1S_0-2s2p\ {}^3P_1^\circ$ has been observed in the first spectrum of beryllium. Wavelength measurements give 4548.538±.002 A, which agrees with the predicted value of 4548.29±.4 A. The energy of the ${}^3P_1^\circ$ level is thus determined to be 21,978.92±.01 K above the ground state, and the value x to be added to all of the triplet terms of Be I tabulated in "Atomic Energy Levels" is −1.18 K. Intensity measurements show that the intensity ratio of the singlet resonance line Be I 2348.61 A, to the intersystem line is about 3×10^7.

1. Introduction

In atomic or ionic spectra displaying two or more systems of terms differing in multiplicity, intersystem transitions are forbidden by the selection rules for pure *LS* coupling. However, the coupling is never strictly pure, and intersystem transitions of considerable intensity have been observed in many spectra, thus fixing the values of all derived spectral terms relative to the zero-energy ground state. If intersystem transitions are not observed, the values of a term system, not including the ground state, will remain uncertain relative to that state by a constant amount, x. Examples of such uncertainties are found in the first two volumes of Atomic Energy Levels [1].[1]

Intersystem transitions produce fairly strong lines in spectra of the heavy elements but become progressively weaker in the spectra of light elements. The intersystem combination ${}^1S_0-{}^3P_1^\circ$ in He I was first detected at 591 A in 1924 by Lyman [2] and later confirmed by Hopfield [3], by Paschen [4], and by Suga [5]. The intensity of this line according to Hopfield [3] and Suga [5] is comparable with that of ${}^1S_0-8\ {}^1P_1^\circ$ or ${}^1S_0-9\ {}^1P_1^\circ$, although Suga [5] says that in a continuous discharge in a water-cooled tube containing helium at 7 mm (Hg) pressure it is comparable with the third or fourth member of this singlet series. In any case, the intensity of the intersystem transition is only a small fraction of that characteristic of 584 A, the first line of this series.

The transitions, ${}^1S_0-{}^3P_1^\circ$, in analogous Li II, Be I, B II, C III, N IV spectra have not been observed. In the case of Be I, the wavelength of this resonance line was first calculated from series limits by Paschen and Kruger [6] to be 4547.88±0.4 A, and later when Paschen [7] revised the limit of the singlet series he predicted the wavelength should be 4548.29 A. In 1929 Paton and Nusbaum [8] reported a line at 4553.07 A to which they assigned this classification, but their result is far beyond the uncertainty quoted above and has not been confirmed. The intersystem resonance line $2s^2\ {}^1S_0-2s2p\ {}^3P_1^\circ$ of Be I has been observed by the present authors, who here report the measured wavelength and estimated relative intensity.

[1] Figures in brackets refer to literature references at the end of this paper.

2. Experimental Procedure

The observation of extremely weak lines, such as the intersystem resonance line of Be I, requires an intense light source free from molecular bands and other spectral background and an efficient spectrograph of high linear dispersion. The light source adopted in this case was a 5-amp d-c arc between pure beryllium electrodes. To eliminate Be O bands that lie in the violet region under observation the source was operated in an enclosure [9] filled with helium. The arc was focused on the slit of a stigmatic concave-grating spectrograph [10]. An excellent 30,000-line/in. grating ruled by R. W. Wood produces a first-order spectrum with a reciprocal dispersion of 2.18 A/mm at 4550 A. A 25-micron slit was used, and a glass filter was placed in front of the slit to absorb the overlapping second-order spectrum. The Be I intersystem line was photographed on Eastman 103–O plates with exposures of 20 to 100 min. When the arc is operated in air, this line is lost in the bands of Be O.

To make sure that the observed line was not a false line produced by the grating, a second series of exposures was made with a large quartz-prism spectrograph having a reciprocal dispersion of 6.3 A/mm at 4550 A. The existence of the line was confirmed in these spectra.

3. Experimental Results

The spectrum line produced by the intersystem combination is shown in figure 1 just to the left of the fifth left-side ghost of Be I, 4572.67 A. The average of four measurements on two grating spectrograms is 4548.538±.002 A. This is within the uncertainty of the predicted value 4548.29±.4 A [7]. The energy of the $2s2p\ {}^3P_1^\circ$ level is thus determined to be 21,978.92±.01 K [2] above the ground state and the value x to be added to all of the triplet terms of Be I tabulated in Atomic Energy Levels [1] is −1.18 K.

An attempt was made to determine the intensity of the intersystem line relative to the more prominent lines of Be I. On the assumption of photographic reciprocity of time and intensity, a series of

[2] In accordance with the recommendation of the Joint Commission for Spectroscopy, the name "kayser" is used for the unit of wave number, 1 K=1 cm^{-1}.

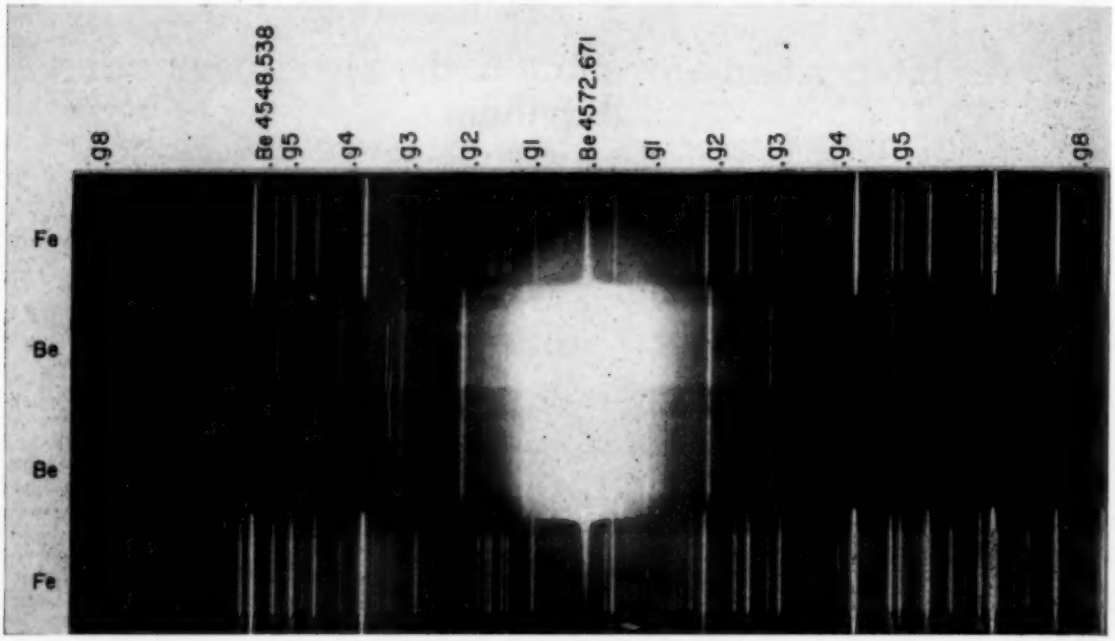

FIGURE 1. *Intersystem resonance line* Be I, 4548.538 A.

timed exposures indicated that the ratio of the intensity of the parent line to the fifth ghost from this grating was about 100,000. From a comparison of the intersystem line with the ghosts of Be I, 4572.67 A, the intensity ratio $\frac{I_{4572.67A}}{I_{4548.54A}}$ is about 400,000. Data taken from standardized arc spectrograms of Be diluted in Cu to eliminate self-absorption show that the intensity ratio of the ($2s^2\,{}^1S_0$—$2s2p\,{}^1P_1^\circ$) resonance line, Be I, 2348.61 A, to ($2s2p\,{}^1P_1^\circ$—$2s3d\,{}^1D_2$) Be I, 4572.67 A is about 70. Therefore, the experimentally determined ratio of the intensity of the singlet resonance line to that of the intersystem is about 3×10^7.

Assuming that the number of atoms in any excited level is determined by the Boltzmann distribution, the theoretical ratio is [11, 12]

$$r=\frac{9}{2}\left[\frac{(^1P_1)-(^1S_0)}{(^3P_1)-(^1S_0)}\right]^4\left[\frac{(^1P_1)-(^3P_1)}{(^3P_2)-(^3P_0)}\right]^2 \exp\left[-\frac{1.439[(^1P_1)-(^3P_1)]}{T}\right],$$

where the levels in parentheses indicate the corresponding energy in kaysers. The temperature, T, is in degrees Kelvin. For an arc temperature of 5,000° K, the calculated value of the intensity ratio is 8×10^6. By use of the parameter λ introduced by King and Van Vleck [11] (assuming the value $\lambda=0.8$, which is an average value in the heavy elements), the calculated ratio is increased to 1.2×10^7. For light elements such as Be, one must also consider the effects of spin-spin and spin-other-orbit interactions on the intensity ratio, which can be done approximately by replacing the difference $(^3P_2)-(^3P_0)$ by $2(^3P_2)+(^3P_0)-3(^3P_1)$. This correction reduces the calculated value to 7×10^6. The calculation is most sensitive to the value assumed for the temperature; a 10-percent change in T will alter r by a factor on the order of 2.

The difference between the calculated value (7×10^6) and the experimental value (3×10^7) may be outside the limits of experimental error, but better agreement could hardly be expected in view of the untested assumptions.

4. References

[1] C. E. Moore, Atomic energy levels, NBS Circ. 467, **I** (1949) **II** (1952).
[2] T. Lyman, Astrophys. J. **60,** 1 (1924).
[3] J. J. Hopfield, Astrophys. J. **72,** 133 (1930).
[4] F. Paschen, Sitz. ber. deu. Akad. Wiss. Berlin, **30,** 662 (1929).
[5] T. Suga, Sci. Pap. Inst. Phys. Chem. Res. (Tokyo) **34,** 16 1937).
[6] F. Paschen and P. G. Kruger, Ann. Physik [5] **8,** 1005 (1931).
[7] F. Paschen, Ann. Physik [5] **12,** 509 (1932).
[8] R. F. Paton and R. E. Nusbaum, Phys. Rev. **33,** 1093 (A) (1929).
[9] H. D. Curtis, J. Opt. Soc. Am. and Rev. Sci. Instr. **8,** 697 (1924).
[10] W. F. Meggers and K. Burns, BS Sci. Pap. **18,** 191 (1922) S441.
[11] G. W. King and J. H. Van Vleck, Phys. Rev. **56,** 464 (1939).
[12] P. J. Rubenstein, Phys. Rev. **58,** 1007 (1940).

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Synthesis of Lactose-1-C^{14} and Lactobionic-1-C^{14} Delta Lactone From 3-β-D-Galactopyranosyl-α-D-Arabinose[1]

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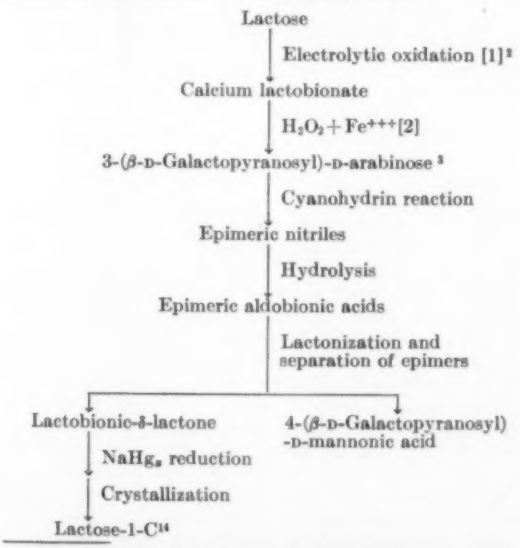
Lactose-1-C^{14}, which has been prepared for the first time, was obtained in 38-percent radiochemical yield by the cyanohydrin synthesis with 3-(β-D-galactopyranosyl)-D-arabinose. The latter substance was prepared in crystalline form and its reaction with $NaC^{14}N$ was studied under a variety of conditions. Acid catalysts favor production of the epimer having the mannose configuration. An improved procedure is given for the lactonization of lactobionic acid; by slow crystallization from methyl cellosolve, large crystals of high-purity lactobionic-1-C^{14} delta lactone were obtained. The lactone was reduced to lactose by sodium amalgam in the presence of sodium acid oxalate with a yield (by analysis) of 84 percent. A modification of the process in which the separation of the epimeric acids or lactones is omitted, was also found to be practicable for the production of lactose-1-C^{14}.

1. Introduction

There are many unsolved problems in human and animal nutrition that can be attacked by means of certain position-labeled carbohydrates. Lactose, one of the most important of these carbohydrates, has not heretofore been available in radioactive form. This paper reports the preparation of high-activity 1-C^{14}-labeled lactose in good yield by means of a cyanohydrin synthesis on 3-galactosyl-arabinose.

2. Discussion of the Experimental Method

The over-all plan for the production of labeled lactose consisted of the following steps:



To provide a basis for directing the cyanohydrin reaction to lactobionic nitrile rather than to 4-galactosyl-mannonic nitrile, the condensation of 3-galactosyl-arabinose with cyanide was studied by means of a tracer technique. This involved condensation of the sugar with labeled cyanide in buffered solutions, hydrolysis of the cyanohydrins, and separation of the labeled lactobionic acid as the calcium lactobionate calcium bromide double salt [4]. It was found that sodium bicarbonate and presumably other general acid catalysts in the cyanohydrin mixture favor formation of the 4-galactosyl-mannonic epimer; calcium chloride or sodium carbonate, however, favor formation of the 4-galactosyl-gluconic (lactobionic) epimer. These results obtained by tracer methods, correspond qualitatively to those obtained by optical rotation and isolation methods in the study of the cyanohydrin synthesis for the production of D-glucose-1-C^{14} and D-mannose-1-C^{14} from D-arabinose [5]. In the preparation of labeled lactose, both the calcium chloride method [6], and the sodium carbonate method for conducting the cyanide condensation were used, but the latter is preferable because it avoids the introduction and subsequent troublesome removal of the chloride ion. In early preparations by the calcium chloride method, lactobionic acid was isolated from the cyanohydrin hydrolyzate as the crystalline calcium lactobionate calcium chloride double salt [7]. The procedure involved several steps later eliminated by condensation in the presence of sodium carbonate, and crystallization of lactobionic lactone from the hydrolyzate. The latter step was made practicable by the development of a procedure for the complete conversion of lactobionic acid to the lactone.

To ascertain favorable conditions for reduction of the lactone to lactose, numerous samples of nonradioactive lactobionic delta lactone were reduced with various quantities of sodium amalgam in the presence of sodium acid oxalate. The reduction was conducted in the apparatus described previously [5], but modified by a sidearm that permitted addition of amalgam while the solution was being stirred. It was found by analysis that, under suitable conditions, 84 percent of the lactone is converted to the sugar.

[1] Part of a project on the development of methods for the synthesis of radioactive carbohydrates, sponsored by the Atomic Energy Commission.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] The alpha modification of this sugar, 3-(β-D-galactopyranosyl)-α-D-arabinose had been crystallized several years ago by Zemplén [3], but no seed crystals were available in this laboratory. However, after about 2 months, crystals were obtained from a sirup containing methyl cellosolve and isopropyl ether. Thereafter, crystallization of other preparations was readily effected by use of seed crystals.

After removal of sodium salts, the lactose was separated by crystallization from aqueous methanol with the addition of isopropanol. In radioactive preparations, additional labeled sugar was recovered from the mother liquor by the carrier technique. In a preparation starting with 3.5 mc of C^{14}-labeled sodium cyanide the yield of labeled lactobionic delta lactone was 54 percent. In the reduction step 68 percent of the lactone was isolated as crystalline lactose. The over-all radiochemical yield of lactose-1-C^{14} was thus 37 percent.

It was also found practicable to prepare lactose without the separation and purification of any intermediate, by reducing the crude lactone mixture prepared from the cyanohydrin reaction. The resulting solution gave one crop of crystalline lactose without carrier; additional crops, obtained by use of carriers, raised the radiochemical yield to 38 percent.

3. Experimental Details

3.1. Preparation of 3-(β-D-Galactopyranosyl)-α-D-Arabinose

A mixture of 375 g of calcium lactobionate pentahydrate, 20 g of barium acetate monohydrate, and 10 g of ferric sulfate (with about $6H_2O$), was added to 3 liters of boiling water [2]. The mixture was cooled to 35° C, and 120 ml of 30-percent hydrogen peroxide was added. During the ensuing reaction period, the solution was cooled to maintain a temperature of less than 50° C. After about 1 hr the solution, which had turned dark brown, was cooled to 40° C, and a second 120-ml portion of hydrogen peroxide was added. When the second reaction was complete, about 25 g of a decolorizing carbon and 10 g of calcium carbonate were added. The mixture was filtered, and the filtrate was evaporated under reduced pressure to a sirup of about 80-percent total solids. The sirup was mixed first with 300 ml of methanol, and then 600 ml of a 1:1 mixture of methanol and ethanol was added. The resulting precipitate was separated by filtration, and was washed, first on the filter, then in a beaker, and finally on the filter with a total of 500 ml of ethanol. The residue was discarded. The filtrate and wash liquor deposited some gummy material from which the clear liquid was decanted. The residue was triturated with 100 ml of ethanol, and the ethanol extract was filtered. The solid was discarded and the filtrate, combined with the alcoholic solution previously separated by decantation, was evaporated under reduced pressure to a sirup of about 90-percent total solids. The sirup was then extracted by trituration successively with two 200-ml portions of methanol and two 200-ml portions of isopropanol; the residue was discarded. The alcoholic extracts were combined and allowed to stand at room temperature for further separation of gummy impurities. When the supernatant liquid had become clear, it was decanted from the residue and evaporated under reduced pressure to a thick sirup. This was dissolved in water, and the solution was passed over a column (2 by 30 cm) containing a mixture of cation and anion exchange resins.[4] The combined effluent and wash liquor was evaporated under reduced pressure to a thick sirup, which was dissolved in about 50 ml of methyl cellosolve. From this solution several fractions of sirupy 3-galactosyl-arabinose were precipitated by the addition of isopropyl ether. Each of the fractions was dissolved in methyl cellosolve and the solutions, brought to incipient turbidity by means of isopropyl ether, were stored in a desiccator over calcium chloride. After 2 months, the sirupy residue of one fraction crystallized. The remaining fractions crystallized when seeded, and a total of 50 g of crude crystalline 3-(β-D-galactopyranosyl)-α-D-arabinose was obtained. To recrystallize, the material was dissolved in a minimum of hot water, and the solution was filtered with the aid of decolorizing carbon and treated with isopropanol almost to the point of turbidity. It was also recrystallized from a thick aqueous sirup (80° Brix) by the addition of methyl cellosolve. $[\alpha]_D^{20}$ of the purified product was −62.5° at equilibrium (water, $c=2$) in approximate agreement with the value previously reported by Zemplén [3] ($[\alpha]_D^{20}=-50.3°\rightarrow-63.1°$).

3.2. Epimeric Proportions of the Products Formed by Condensation of 3-(β-D-Galactopyranosyl)-D-arabinose with Cyanide

The experiments outlined in table 1 were conducted to determine optimum conditions for the formation of the lactobionic epimer. In each experiment 2 ml of a solution containing 0.0636 millimole of C^{14}-labeled cyanide with 5.12 μc of activity was placed in a glass-stoppered tube. The solution was frozen in a carbon dioxide-acetone freezing mixture to prevent loss of cyanide, after which 2 ml of a solution, containing 0.0705 millimole of 3-galactosyl-arabinose and the various substances listed in table 1, was introduced. The mixture was shaken gently until the ice dissolved and was then allowed to stand at room temperature. After 48 hr, the mixture was heated at 80° C for 5 hr to effect hydrolysis, and then was evaporated to dryness in an air stream. The residue in each tube was dissolved in a few drops of water, and the solution was neutralized to the end point of phenolphthalein by the addition of dilute hydrobromic acid. Nonradioactive calcium lactobionate calcium bromide (531.3 mg of Ca $(C_{12}H_{21}O_{12})_2.CaBr_2.6H_2O$) [4] was dissolved in each hydrolyzate, and the solutions were concentrated to thick sirups in a stream of air. Each of the sirups was diluted with 50-percent aqueous isopropanol to a volume of about 2 ml. Any turbidity that developed during the dilution was discharged by the dropwise addition of water, and the solutions were finally treated with isopropanol to incipient turbidity, and were seeded with the double salt. As crystallization proceeded, additional isopropanol was added. After 72 hr, the mother liquor was removed with a capillary pipette, and the crystals were washed with 50-percent aqueous isopropanol. The labeled

[4] The cation exchange resin was Amberlite IR100, analytical grade, Resinous Products Division of Rohm & Haas Co., Philadelphia, Pa.; the anion exchange resin was Duolite A-4, Chemical Process Co., Redwood City, Calif.

compound from each experiment was recrystallized from concentrated aqueous solution by the method described above. Samples of the recrystallized calcium lactobionate calcium bromide were dried over calcium chloride, and their carbon-14 content was determined by direct count in formamide solution [8]. A 22.2-mg sample of the product from experiment 1, dissolved in 1 ml of formamide gave 41.1 c/s in a proportional counter, in which 1 c/s is equivalent to 0.00241 μc. A 20.6-mg sample of the product from experiment 2 gave 20.5 c/s. These values correspond to 0.00446 and 0.00240 μc/mg, respectively.

Table 1. *Epimeric proportions in the condensation of 3-galactosyl-D-arabinose with cyanide*

Experiment	Reaction mixture		Activity of purified carrier $Ca(C_{12}H_{21}O_{12})_2CaBr_2.6H_2O$		Lactobionic epimer[d]
		Millimoles	μc/mg	μc/milliequivalent of lactobionate	*Percent*
1	NaCN	[a] 0.0636	0.00446	2.37	47.7
	Na_2CO_3	.06			
	3-Galactosyl-arabinose	.0705			
2	NaCN	[a] .0636	0.00240	1.28	25.3
	$NaHCO_3$	.06			
	CO_2	[b] Saturated			
	3-Galactosyl-arabinose	0.0705			

[a] Contained 5.12 μc of carbon-14, or 80.5 μc/millimole.
[b] A piece of CO_2 ice, the size of a pea, was added after the cyanide solution had been frozen.
[c] 531.5 mg of $Ca(C_{12}H_{21}O_{12})_2.CaBr_2.6H_2O$ (1 milliequivalent of lactobionate) was added to the reaction mixture.
[d] Percentage of lactobionic epimer $=(A_2/(A_1-A_2))(100/0.0636)$, where A_1 and A_2 are, respectively, the activities per milliequivalent of the lactobionate formed and the lactobionate isolated.

3.3. Lactonization of Lactobionic Acid, and Crystallization of the Delta Lactone [9]

Because complete conversion of lactobionic acid to the lactone is difficult, a series of experiments was conducted to ascertain suitable conditions for the quantitative production of the lactone on a millimole scale. The following procedure was found to be satisfactory: An aqueous solution of the acid was mixed with an equal volume of methyl cellosolve and was lactonized by gradual evaporation of the solvent under a stream of dry air at room temperature, in the presence of seed crystals of lactobionic delta lactone. After the material had been concentrated to a semisolid mass, it was stored in a desiccator over calcium chloride, with the addition from time to time of sufficient methyl cellosolve to keep it moist. At the end of a week, the addition of methyl cellosolve was discontinued, and the material was stored at room temperature over calcium chloride for a week or longer. The product was recrystallized by dissolving it in 50 parts of methyl cellosolve at 95° to 100° C. The solution was filtered and concentrated under reduced pressure in the presence of seed crystals. When a satisfactory crystallization had occurred, the mother liquor was separated by use of a capillary pipette, and the crystals were washed with methyl cellosolve. By concentration of the mother liquors nearly all of the material was recovered. The melting point of the product, 199° to 205° C. is somewhat dependent upon the rate of heating. The value found in the present study is noticeably higher than the melting point (196° to 197° C.) previously reported [9].

3.4. Reduction of the Lactobionic Lactone with Sodium Amalgam in the Presence of Sodium Acid Oxalate

To provide a basis for the efficient reduction of lactobionic lactone, the reductions outlined in table 2 were conducted in the apparatus of figure 1. In each case 0.5 millimole of crystalline lactone was placed in the apparatus together with the oxalic acid and sodium oxalate listed. Ten milliliters of ice water was then added and, after the stirrer had been started,

Table 2. *Reduction of lactobionic delta lactone [a] by sodium amalgam in the presence of oxalate buffers*

Experiment	Sodium oxalate	Oxalic acid	$NaHg_2$[b]	Yield of lactose (by analysis)
	g	*g*	*g*	*Percent*
1	0.10	0.09	0.6	80.3
2	.20	.18	1.2	84.2
3	.40	.35	2.3	82.7
4	.80	.70	4.6	80.0
5 [c]	.80	.70	4.6	79.3
	.80	.60	4.6	
6 [d]	.80	.70	4.6	78.9
	.80	.60	4.6	

[a] 0.5 millimole in 10 ml of water.
[b] 5-percent amalgam.
[c] The second quantity of amalgam and buffer were added after the first had completely reacted.
[d] Three successive additions of amalgam and buffer were used.

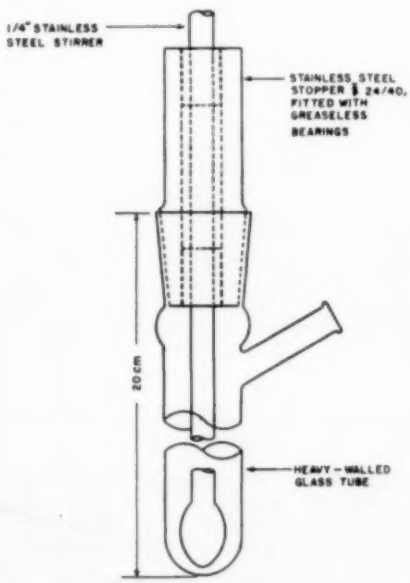

1/4" STAINLESS STEEL STIRRER
STAINLESS STEEL STOPPER § 24/40, FITTED WITH GREASELESS BEARINGS
20 cm
HEAVY-WALLED GLASS TUBE

Figure 1. *Sodium amalgam reduction apparatus.*

the indicated quantity of sodium amalgam pellets was added through the sidearm. The mixture, cooled in an ice bath, was stirred vigorously until the amalgam was spent (about 2 hr). The mercury was removed, and the solution was neutralized by the addition of sufficient sodium hydroxide solution to give a faint permanent pink color with phenolphthalein; this was discharged by dropwise addition of a solution of oxalic acid. A fivefold quantity of methanol was added, and the crystalline salts were removed by filtration, washed with methanol, and discarded. The mother liquor was diluted with water to exactly 100 ml, and 10-ml aliquots were transferred to flasks for analysis by the modified Scales method [10]. Before analysis, the alcohol was removed from each sample by evaporation in an air stream, and the residue was dissolved in the requisite amount of water (10 ml).

For the isolation of lactose, the reduction was carried out as described in the preceding paragraph, and with the proportions of materials given in experiment 2 of table 2. After removal of the salts by filtration, the alcoholic filtrate was concentrated to a thin sirup under reduced pressure, a fourfold quantity of methanol was added, and the small crop of salts thus precipitated was immediately separated.[5] The methanol in the filtrate was removed by evaporation, the product was diluted with water, and the solution was passed over a column of mixed cation and anion exchange resins (about 20 ml). The resin was washed with water until the activity of the effluent was negligible, and the combined solution and washings were concentrated under reduced pressure, and finally were lyophilized (freeze-dried). The residue, dissolved in a few drops of water, was immediately transferred to a tared test tube, and the solution was seeded, and treated with methanol to incipient turbidity. Isopropanol was added as crystallization proceeded, and the material was finally stored for several days in a refrigerator. The mother liquor was then removed by means of a capillary pipette, and the crystals were washed with a methanol-isopropanol mixture (2:1). To recrystallize, the lactose was dissolved in a minimum amount of hot water; the solution was filtered with the aid of a decolorizing carbon, and the filtrate was concentrated, if necessary, and treated with methanol and isopropanol in the presence of seed crystals. When crystallization appeared to be complete, the mother liquor was removed, and the crystals were washed with methanol-isopropanol mixtures, and finally dried in a vacuum desiccator over calcium chloride.

3.5. Preparation of Lactobionic-1-C^{14} delta Lactone and Lactose-1-C^{14}

To a small flask containing 343 mg (1 millimole) of 3-galactosyl-arabinose and 84 mg of sodium bicarbonate, there was added at ice temperature 5 ml of a solution containing 1 millimole each of sodium hydroxide, and of C^{14}-labeled sodium cyanide with 3.5 mc of activity. The flask was sealed and allowed to stand at room temperature for 3 days. The resulting cyanohydrins were then hydrolyzed by heating the mixture at 70° C for 6 hr in the presence of an air stream. Water was replaced from time to time, and at the end of the period the solution was allowed to evaporate to dryness. The residue, dissolved in 50 ml of water, was passed through a column of cation exchange resin, which was then washed until no appreciable activity remained.

The combined solution and washings were concentrated under reduced pressure to a sirup. The material was transferred by means of 2 ml of water to a test tube, lactonized by the method described in section 3.3, and recrystallized from hot methyl cellosolve. In order to remove the residual labeled lactone from the mother liquor by the carrier technique, several quantities of nonradioactive lactobionic lactone were employed. These were successively crystallized from the mother liquor in the manner previously described, and recrystallized before analysis. The quantities and radiochemical yields are given in table 3.

The crops of lactobionic lactone listed in table 3 were reduced in three portions. Before reduction, the 53-mg quantity of lactone obtained without carrier was combined with the first two carrier crops.

TABLE 3. *Summary of radiochemical yield of lactobionic-1-C^{14} delta lactone from 3.5 millicuries of* $NaC^{14}N$

Crop	Lactone added as carrier	Lactone isolated	Activity
	mg	*mg*	*μc*
1	None	52.5	486
2	200	165	379
3	200	120	217
4	500	338	248
5	500	630	567
Total			1,897
Radiochemical yield			54.2%

TABLE 4. *Summary of radiochemical yield of lactose-1-C^{14} from lactobionic-1-C^{14} delta lactone*

Lactone reduced		Lactose added as carrier	Lactose-1-C^{14} isolated
mg	*μc*	*mg*	*μc*
331.4	1,082	---	448
338.0	248	---	189
630	567	---	468
---	---	500	109
---	---	500	59
---	---	500	23
Total	1,897	---	1,296
Radiochemical yield from lactone			68.4%
Over-all radiochemical yield [a]			37.2%

[a] From 3.5 millicuries of $NaC^{14}N$.

[5] This precipitate generally contained some sodium lactobionate. It was saved for treatment with a later preparation. Delay in removal of the salts may allow crystallization of the sugar to occur.

In each case, the reduction was conducted in the manner described in section 3.4 and with quantities of material proportional to those of experiment 2 of table 2. After the first crop of lactose had been removed, three 500-mg quantities of nonradioactive lactose were used successively as carriers, by crystallization from the mother liquor. The results of this preparation are given in table 4. It will be seen that the radiochemical yield of lactose from lactobionic delta lactone was 68.4 percent. The over-all radiochemical yield from labeled sodium cyanide was 37 percent.

3.6. Preparation of Lactose-1-C^{14} without Isolation of Intermediates

A cyanohydrin synthesis was conducted by the carbonate method with 2 millimoles of 3-galactosyl-arabinose, and 2 millimoles of labeled cyanide containing 28.3 μc of activity. After hydrolysis of the cyanohydrins, cations were not removed, but sufficient oxalic acid was added to the solution to convert the sodium ion present to sodium acid oxalate. The solution was evaporated to dryness repeatedly in the presence of aqueous methyl cellosolve and seed crystals of lactobionic lactone. Finally, the material was stored in a desiccator and moistened from time to time with methyl cellosolve. At the end of 2 weeks, the amalgam reduction was carried out by the method described in section 3.4, but allowance was made for the amount of oxalate in the mixture. The first crop of crystalline lactose contained 7.5 μc of activity, and carrier crops containing 3.4 μc brought the total yield to 10.8 μc, or 38.0 percent. Although this method is less laborious than the preparation described in section 3.5, extreme care must be observed in the purification of the lactose because the crude product contains a higher proportion of radioactive contaminants than the lactose from a purified lactobionic lactone.

3.7. Preparation of Sodium Lactobionate-1-C^{14}

After the work reported in the preceding sections was completed, F. H. Stodola of the Northern Regional Research Laboratory, United States Department of Agriculture, Peoria, Ill., kindly supplied a sample of crystalline sodium lactobionate [11].

To provide a supply of sodium lactobionate-1-C^{14}, 1 millimole of 3-galactosyl-arabinose was reacted with C^{14}-labeled cyanide, as described in section 3.5. The reaction mixture from the cation exchange resin was neutralized with sodium hydroxide, to a phenolphthalein end point. A small quantity of decolorizing carbon was added, and the solution was filtered and evaporated to a sirup. Methanol was added to the point of incipient turbidity, and the mixture was seeded with crystalline sodium lactobionate. After several days labeled sodium lactobionate was separated. The product was recrystallized from water by the addition of methanol. The salt crystallizes well and is easily purified. The yield without carrier was 40 percent of the theoretical; by use of carrier a radiochemical yield of 50 percent was obtained.

4. References

[1] H. S. Isbell and H. L. Frush, BS J. Research **6,** 1145 (1931) RP328.
[2] O. Ruff and G. Ollendorff, Ber. deut. chem. Ges. **33,** 1798 (1900); R. C. Hockett and C. S. Hudson, J. Am. Chem. Soc. **56,** 1632 (1934).
[3] G. Zemplén, Ber. deut. chem. Ges. **59,** 2402 (1926); **60,** 1309 (1927).
[4] H. S. Isbell, J. Research NBS **17,** 331 (1936) RP914.
[5] H. S. Isbell, J. V. Karabinos, H. L. Frush, N. B. Holt, A. Schwebel, and T. T. Galkowski, J. Research NBS **48,** 163 (1952) RP2301.
[6] C. S. Hudson, O. Hartley, and C. B. Purves, J. Am. Chem. Soc. **56,** 1248 (1934).
[7] A. Stoll and W. Kussmaul, U. S. Patent 1,648,368 (1927).
[8] A. Schwebel, H. S. Isbell, and J. V. Karabinos, Science **113,** 465 (1951).
[9] H. S. Isbell, BS J. Research **11,** 713 (1933) RP618.
[10] H. S. Isbell, W. W. Pigman, and H. L. Frush, J. Research NBS **24,** 241 (1940) RP1282.
[11] G. E. N. Nelson and F. H. Stodola, J. Am. Chem. Soc. **75,** 1748 (1953).

WASHINGTON, November 6, 1952.

Surface Areas of Cottons and Modified Cottons Before and After Swelling as Determined by Nitrogen Sorption [1]

Florence H. Forziati, Robert M. Brownell, and Charles M. Hunt

Surface areas of cottons differing in variety and maturity, and cottons that had been subjected to various physical and chemical treatments were measured before and after swelling. Swollen cottons were prepared by immersing air-dried cottons in water at room temperature for 24 hours, displacing the water with methanol and the methanol with pentane, and finally drying the fibers. Surface areas were calculated from the quantity of nitrogen adsorbed at −195.8° C.

The specific surfaces of unswollen fibers were less than 1 square meter per gram; those of the swollen fibers ranged from 4 to 148 square meters per gram. Purification and mercerization produced increases in the surface available after swelling; methylenation produced a decrease; ethylamine treatment had no effect. In the early stages of methanolysis, a decrease in the surface available after swelling occurred; in the later stages, an increase.

Although surface area measurements were probably in no instance made on completely swollen fiber, the procedure employed is believed to be useful in evaluating the effects of various treatments on cottons and other cellulose fibers.

1. Introduction

The extent to which the surface area of the cotton fiber increases when the fiber is in contact with water is believed to have an important bearing on the performance of the fiber during processing and use. Hence, as a part of an investigation of the surface properties of cotton fibers, it was desired to obtain reliable surface-area measurements of the fibers both before and after swelling in water.

In earlier work at the National Bureau of Standards [1] [2], the surface area of purified cotton linters, as calculated by the equation of Brunauer, Emmett, and Teller [2] from data on the sorption of nitrogen was found to increase from 0.7 to 47 m^2/g when the linters were swollen in water, subjected to a process of solvent exchange, and carefully dried. This suggested, as had the work of Assaf, Haas, and Purves [3, 4], that the solvent exchange and drying procedure might be used to stabilize cellulose in the expanded condition resulting from swelling, thus making it possible to apply the method of Brunauer, Emmett, and Teller to the measurement of the specific surface of swollen as well as unswollen fibers. The results of such measurements on a number of cottons differing in variety, maturity, and previous history are discussed in this paper.

2. Materials and Methods

The cottons used in this investigation were purified cotton linters; commercial absorbent cotton; 8 raw cottons representing 7 varieties and ranging in maturity from 38 to 96 percent; dewaxed cotton; cotton that had been dewaxed and then purified by open boiling in 1-percent sodium hydroxide solution; cotton that had been dewaxed and then purified by kierboiling in 1-percent sodium hydroxide solution; cotton yarn purified by open boiling in alkali; cotton yarn purified by kierboiling in alkali; dye resistant and full-dyeing methylenated cottons; mature and immature cottons mercerized without tension; cotton yarn treated to reduce the crystallinity of the fiber; hydrocellulose; and 7 methanolyzed cottons. The linters were from the same lot as those used by Hunt, Blaine, and Rowen [1]. The raw cottons were supplied by E. L. Skau, R. A. Rusca, C. F. Goldthwait, and H. O. Smith; the open-boiled and kierboiled yarns by C. F. Goldthwait and H. O. Smith; the hydrocellulose and yarn of reduced crystallinity by C. M. Conrad; the methylenated cottons by C. F. Goldthwait; and the methanolyzed cottons by R. E. Reeves.[3] These cottons are described further in the following section of this paper.

Nitrogen-adsorption measurements were made with an apparatus similar to that described by Emmett [5], using the procedures recommended by Barr and Anhorn [6]. Surface areas were calculated from the adsorption data by methods previously described [2, 5, 7]. In making the calculations, it was assumed that the nitrogen molecule covered an area of 16.2 A^2.

For measurements on unswollen cottons, the air-dried sample was tightly packed into a glass holder, and a sealed glass tube was inserted above the sample to reduce the "dead space." The holder was then sealed and attached to the adsorption apparatus. When the quantity of cotton permitted, 20- to 30-g samples were used for the nitrogen-sorption measurements; when it did not, 2- to 3-g samples were used, with a consequent decrease in the precision of measurement.

For measurements on swollen cottons with their greatly increased surface areas, 1-g samples were employed. The cotton was swollen by immersion in distilled water for approximately 24 hr at room temperature, and then transferred to a sample holder, which was then attached to the apparatus used in the

[1] A report of work done under cooperative agreement with the United States Department of Agriculture and authorized by the Research and Marketing Act. The work was supervised by the Southern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] Members of the staff of the Southern Regional Research Laboratory of the U. S. Department of Agriculture.

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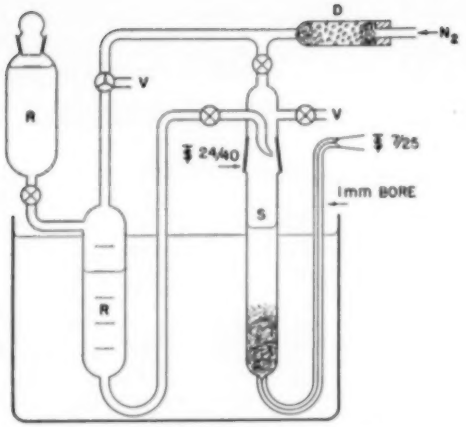

FIGURE 1. *Solvent exchange apparatus.*

R, Solvent reservoirs; V, vents; S, sample holder; D, drying tube.

solvent exchange process (fig. 1). This apparatus was so constructed that liquids were moved by an applied gas pressure on to the sample and subsequently forced through the sample, without the latter at any time being accessible to atmospheric moisture. The water was replaced by anhydrous methanol, which was added in five 10-ml portions, each portion being allowed to remain in contact with the sample for 5 min before being replaced by the succeeding portion. The methanol was replaced by five 10-ml portions of anhydrous pentane in exactly the same way. The sample holder was removed to an ice bath, and the pentane was driven off by a stream of dry nitrogen, 50 ml/min, passing through the sample for 24 hr. A sealed glass tube was then inserted, and the sample holder was sealed off and attached to the nitrogen-sorption apparatus.

Prior to the nitrogen-adsorption measurements, all samples were evacuated until the pressure dropped to between 10^{-5} and 10^{-6} mm of mercury, the sample occupying a position between the pumps and the gage. Evacuation was carried out at room temperature instead of at the higher temperature of 100° to 110° C frequently used in preparing silica gel, bone char, and similar materials for nitrogen-sorption measurements. The lower temperature was considered necessary inasmuch as cotton samples that had been evacuated at 100° to 110° C were found to adsorb slightly less nitrogen than those that had been evacuated at room temperature.

3. Results and Discussion

Before the procedure described above was adopted for the preparation of swollen samples for surface-area measurements, several experiments were carried out on the effect of variations in the procedure used in the earlier work [1]. The purpose of the experiments was to aid in the selection of conditions that would give reproducible data and that would give maximum retention of the expanded structure produced by swelling. As the results of the experiments provide information on the behavior of cotton during swelling and exchange, they are discussed in some detail.

In one set of experiments, surface-area measurements were made on 10 1-g samples of purified cotton linters that had been subjected to the same swelling and dehydration procedure but which differed with respect to the nonpolar liquid used in the exchange process and the conditions under which this liquid was removed. The samples were swollen by immersion in distilled water for 1 hr, dehydrated with methanol, and the methanol replaced with *n*-pentane or benzene as described in the preceding section of this report. After removal of the nonpolar liquid under the conditions shown in columns 3 and 4 of table 1, surface-area measurements were made in the usual way. In some cases, the weight of the sample and holder was recorded at various stages of the process, thus making it possible to determine how completely the liquids used in swelling and exchange had been removed.

The results, given in the last column of table 1, show that the maximum surface area observed, 59 m^2/g, was obtained with the sample from which the nonpolar liquid pentane was removed by a stream of dry nitrogen gas at 0° C. Apparently, the use of low temperature for removing the nonpolar liquid results in less collapse of the expanded cellulose. On the other hand, if the temperature is too low or the liquid is not sufficiently volatile, incomplete

TABLE 1. *Effect of temperature and manner of removal of benzene or pentane on specific surface of swollen cotton linters*

Experiment	Nonpolar liquid	Temperature surrounding sample holder during removal of nonpolar liquid	Method used for removal of nonpolar liquid	Liquid retained (based on original weight of cotton) after—		Specific surface[a]
				Removal of nonpolar liquid	Evacuation and surface area measurement	
				Percent	*Percent*	m^2/g
1	Benzene	Water bath, 20° C.	Dried nitrogen 50 ml/min for 18–24 hr.			47
2	do	Room temperature, 23° to 28° C.	do			46
3	do	Water bath, 30° C.	do			44
4	do	Water bath, 83° to 86° C.	Dried nitrogen 200 ml/min for 15 min.			36
5	do	Room temperature, 23° to 28° C.	Intermittent evacuation with H_2O pump for 1 hr.			52
6	do	Water bath, 30° C.	do			42
7	Pentane	Water bath, 24° C.	Dried nitrogen 50 ml/min for 18 to 24 hr.	0.3		46
8	do	Ice bath, 0° C.	do	.8	0.0	59
9	do	Ice-salt bath, −20° C.	do	2.8	.4	52
10	do	Dry ice, −78.5° C.	Dried nitrogen 50 ml/min for 90 to 96 hr.	5.4	.7	32

[a] Specific surfaces reported in tables 1 to 10, unless otherwise indicated, were calculated from adsorption of nitrogen at −195.8° C, using the equation of Brunauer, Emmett, and Teller.

removal of the liquid with a consequent decrease in available surface is to be expected.

In a second set of experiments, 2-g samples of a commercial absorbent cotton were swollen for varying periods of time by immersion in distilled water at room temperature, by shaking in distilled water at room temperature, and by immersion in boiling distilled water. At the end of the swelling periods, the samples were subjected to solvent exchange and dried (using the standard procedure described in the preceding section), evacuated, and then used for surface-area measurements. The values obtained, presented in table 2 and figure 2, show that specific surface increases rapidly during the first few minutes of contact with water; thereafter, it continues to increase at a much less rapid rate. This suggests that use of very short swelling periods would give results of poorer reproducibility than longer periods. Agitation and heating during swelling are shown to result in increased surface. The results indicate, however, that small fluctuations such as occur in the temperature of the laboratory would have little effect on specific surface. Accordingly, it was assumed that swelling in water at room temperature for 24 hr would give results of satisfactory reproducibility.

The possibility that rapid removal of water from cellulose during solvent exchange might result in collapse of the expanded cellulose is suggested by the biologists' experience in preparing specimens for embedding and sectioning. Kistler [8] failed to find evidence of collapse when rapid dehydration was used in the preparation of aerogels from cellophane. He did not, however, compare the surface areas of aerogels prepared by rapid and by gradual replacement of water. As such a comparison was considered of interest, surface-area measurements were made on two swollen samples of purified cotton whose preparation differed only with respect to the method used to replace the water with absolute methanol. At the end of the swelling period, one sample was transfered to methanol solutions of gradually increasing concentration until absolute methanol was reached. In order that equilibrium be reached in each concentration, several days were allowed for the dehydration process. The second sample was placed in the sample tube at the end of the swelling period and subjected to the usual rapid replacement of water with methanol. In both samples, the replacement of methanol with pentane and the removal of pentane were done in the usual way. As the specific surfaces of the two samples were found to be essentially the same, it was concluded that nothing was to be gained by gradual replacement of water with methanol.

TABLE 2. *Effect of variations in procedure during swelling on specific surface of absorbent cotton*

Time of swelling	Specific surface of the absorbent cotton			
	Sample neither swollen nor exchanged	Sample swollen by immersion in water at room temperature, then exchanged and dried	Sample swollen by shaking in water at room temperature, then exchanged and dried	Sample swollen by immersion in boiling H_2O, then exchanged and dried
	m^2/g	m^2/g	m^2/g	m^2/g
0	0.8			
5 min		5		
		5		
15 min				11
1 hr		7		12
		7	11	10
3 hr				14
20 hr		10	12	
			13	
23 hr				15
46.5 hr				16

As a result of the difficulty encountered in wetting raw cotton with water, the possibility of swelling the cottons in water containing a small amount of a wetting agent, 0.5 percent, then washing with water before subjecting to solvent exchange and drying was considered. Samples prepared in this way usually had lower specific surfaces, irrespective of the nature of the wetting agent, than those swollen in water, thus suggesting that washing failed to remove all of the wetting agent. Accordingly, the use of wetting agents was abandoned.

In table 3 are given the results of specific-surface measurements on swollen and unswollen specimens

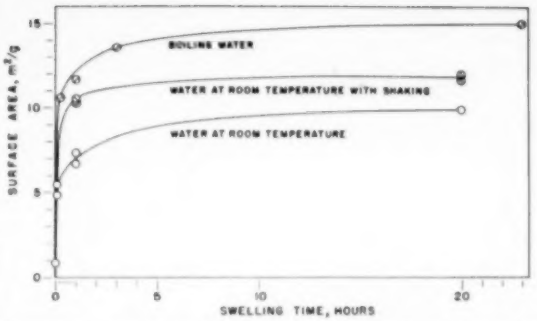

FIGURE 2. *Variation in surface area of absorbent cotton with time of swelling*

TABLE 3. *Specific surface of raw cottons*

Cotton	Maturity	Weight fineness by array *	Specific surface of unswollen cotton by—		Specific surface after swelling in water, followed by solvent exchange and drying by nitrogen sorption
			Aeralometer *	Nitrogen sorption	
	Percent	*μg/in.*	m^2/g	m^2/g	m^2/g
Memphis B/376839	38		0.56	0.8	34
				.6	21
Empire AP845	68	4.1	.31	.6	21
				.7	
				.6	
				.7	
Empire 2B/93	69	4.2	.32	.6	28
					30
Stoneville 2C	82	4.2	.31	.6	
				.8	
Deltapine PC-2790	80	4.3	.29	.5	
				.5	
Lockett 140	93	5.6	.24	.4	26
				.5	23
AHA PC-2868	94	3.8	.27	.3	
Iquitos PC-2867	96	8.0	.19	.3	

* Measurements made by Southern Regional Research Laboratory of the U. S. Department of Agriculture. The results of aeralometer measurements were converted from square millimeters per cubic millimeters to square meters per gram by assuming the density of cotton to be 1.52 g/cm³.

of a number of raw cottons differing in variety, maturity, and weight fineness. The results show that the unswollen cottons varied in specific surface from 0.8 to 0.3 m^2/g with the cottons falling in the order of increasing maturity when arranged in the order of decreasing specific surface. The fact that the values obtained for the specific surfaces of the unswollen cottons are slightly greater than those obtained by the arealometer method [9], also given in the table, is consistent with the thought that the latter method measures only the external surface, whereas the former also measures the lumen and channels within the fiber.

The four cottons measured after swelling in water, solvent exchange, and drying varied in specific surface from 20 to 34 m^2/g. Although the immature Memphis cotton had a greater specific surface than the other swollen cottons, there appears to be no correlation between degree of maturity and the increase in specific surface resulting from treatment with water followed by solvent exchange and drying. In fact, samples taken from two bales of Empire cotton having essentially the same degree of maturity differed in specific surface when swollen by approximately 9 m^2/g.

The results given in table 4 show the effect of various purification treatments on the specific surface of Empire cotton before and after swelling. They indicate that the removal of impurities produces little, if any, change in the specific surface of unswollen cotton. The surface area available after swelling was found to be the same in raw cotton and in cotton that had been dewaxed by extraction with boiling ethanol for 6 hr; in cotton that had been dewaxed and then freed of pectic substances by boiling in 1-percent sodium hydroxide in the absence of air for 2 hr, the surface area increased approximately 24 m^2/g, an increase of 110 percent. Removal of pectic substances by autoclaving at 120° C in 1-percent sodium hydroxide solution for 2 hr [4] resulted in an increase of approximately 7 m^2/g or 33 percent. As the wax is believed to be confined to the outer surface, whereas the pectic substances are distributed throughout the fiber, it is not surprising that removal of pectic substances should have a greater effect on the specific surface of the swollen fiber than does removal of wax. Why removal of the impurities at atmospheric pressure should result in a greater increase than removal under increased pressure is unknown. That the use of increased pressure during purification does give a lesser increase in the surface available after swelling is further suggested by the results of surface-area measurements on yarns that had been purified by open-boiling in 2-percent sodium hydroxide solution for 2 hr and by kierboiling in 2- to 3-percent sodium hydroxide solution for 6 hr at 120° C, respectively, then swollen in water containing 0.5-percent Aerosol OT, washed with water, exchanged, and dried in the usual manner. These results are shown in table 5. It is of interest that Gailey [10] found the barium hydroxide sorptive capacity of kierboiled cottons to be less than that of cottons purified by boiling for 1 hr in 1-percent olive oil soap containing 0.2 percent of sodium carbonate. He attributed the decrease in sorptive capacity to increased crystallinity.

Specific-surface measurements obtained on two partially methylenated cottons prepared by reaction of an acetone solution of formalin with raw cotton [11] are shown in table 6. Both products contained approximately 0.3 percent of formaldehyde, but one was prepared from air-dried cotton, the other from cotton that had been wet with water and then squeezed free of excess water. The former product was resistant to dyeing with direct dyes, whereas the latter resembled the original cotton in dyeing behavior. Both the dye-resistant character of this methylenated cotton, and the relatively small increase in specific surface, around 3 m^2/g, produced by swelling and exchange of the methylenated product from air-dried cotton, support the conclusion that the formaldehyde is present in the form of crosslinks that interfere with swelling [11, 12]. The larger increase in specific surface, approximately 19 m^2/g, produced by swelling of the methylenated product from prewet cotton indicates that the position of the crosslinks in this product is such that the cotton retains much but not all of its swelling ability. That these crosslinks do not serve to hold the cellulose in the expanded condition is shown by the fact that the spe-

TABLE 4. *Effect of purification on specific surface of cotton*

Cotton	Specific surface of unswollen cotton	Specific surface after swelling in water, followed by solvent exchange, and drying
	m^2/g	m^2/g
Empire AP845, raw	0.6	21
	.6	21
	.7	----------
	.6	----------
	.7	----------
Empire AP845, after extraction with boiling ethanol	.5	21
	.6	21
Empire AP845, after extraction with boiling ethanol followed by boiling in 1% NaOH for 4 hr in absence of air	.7	48
	.7	45
Empire AP845, after autoclaving in 1% NaOH at 120° C for 2 hr	------	28
		24

TABLE 5. *Effect of method of purification on specific surface of cotton yarn*

Yarn	Specific surface of unswollen cotton [a]	Specific surface after swelling in 0.5-% aerosol OT, followed by washing in water, solvent exchange, and drying
	m^2/g	m^2/g
Series 2, Empire B/92, purified by open scouring	0.6	27
		25
Series 2, Empire B/92, purified by kierboiling	.6	16
	.4	16

[4] The sample purified according to this procedure was supplied by R. E. Reeves of the Southern Regional Research Laboratory, U. S. Department of Agriculture.

[a] As 2- to 3-g. samples were used for these measurements, the values obtained are regarded as approximate.

cific surface on the unswollen, partially methylenated product prepared from prewet cotton is of the same order of magnitude as that of the original cotton—less than 1 m^2/g.

In table 7 are given the results of specific-surface measurements on swollen and unswollen specimens of a mature Lockett cotton and an immature Memphis cotton before and after mercerization without tension for 10 min in 20-percent sodium hydroxide solution at 20° C. Although the measurements on the unswollen mercerized cottons were made on 2- to 3-g samples and are thus to be regarded as only approximate, they suggest that mercerization results in a decrease in the surface available before swelling. However, the area available to nitrogen after swelling, exchange, and drying increased on mercerization from approximately 25 to 100 m^2/g for the mature Lockett cotton and from 34 to 148 m^2/g for the immature Memphis cotton. That mercerization would result in an increase in the surface available after swelling is to be expected from published observations that mercerization of cotton without tension results in increased sorption of moisture [13, 14] and of alkalis [10, 15] and dyes [16] from aqueous solution. Exact interpretation of the results, however, is made difficult by the fact that several changes that might influence the swelling behavior of the fiber occur during mercerization. In addition to the conversion of the water-impermeable crystal lattice of cellulose I to the water-permeable crystal lattice of cellulose II [17], decreases occur in the total amount of crystalline cellulose, crystallite size, orientation, and degree of polymerization.

Segal, Nelson, and Conrad [18] have shown that treatment of cotton with alkylamines results in decreases in degree of crystallinity and crystallite size, and an increase in moisture sorption. As swelling is believed to be confined to the amorphous regions, it was assumed that alkylamine treatment would result in an increase in the surface available to nitrogen after swelling, exchange, and drying. The results given in table 8 show, however, that reduction of the crystallinity of cotton yarn from 90.8 ± 1.6 percent to 43.3 ± 10.7 percent by treatment for 4 hr with ethylamine in the cold and under nitrogen produced little if any change in the surface available to nitrogen both before and after swelling. A possible explanation is that the crystalline regions, although reduced in size, are present in sufficient number to limit the movement of cellulose chains as they pass through the enlarged amorphous regions, thereby preventing increased swelling of these regions.

Unexpected results (table 9) were also obtained when surface-area measurements were made on hydrocellulose prepared by the reaction of lightly kiered and bleached cotton with 2.5-molar hydrochloric acid for 4 hr at 100° C. As hydrolysis is believed to result in the removal of the amorphous

TABLE 6. *Effect of methylenation on specific surface of cotton*

Cotton	Formaldehyde content [a]	Color produced with direct blue dye [a]	Specific surface of unswollen cotton	Specific surface after swelling in water, followed by solvent exchange and drying
	Percent		m^2/g	m^2/g
Empire B/92	------	Full blue	[b] 0.6	30
				28
Methylenated cotton (157) prepared from air-dried Empire B/92.	0.31	Blue-white	.8	2
			.8	6
Methylenated cotton (158) prepared from prewet Empire B/92.	.26	Full blue	[b] .5	19
			[b] .5	19

[a] Data supplied by C. F. Goldthwait, of the Southern Regional Research Laboratory, U. S. Department of Agriculture.
[b] As 2- to 8-g samples were used for these measurements, the values obtained are regarded as approximate.

TABLE 7. *Effect of mercerization without tension on specific surface of cotton*

Cotton	Specific surface of unswollen cotton	Specific surface after swelling in water, followed by solvent exchange and drying
	m^2/g	m^2/g
Memphis B/376839, not mercerized	0.8	34
Memphis B/376839, completely mercerized without tension	[a] .2	148
Lockett 140, not mercerized	.4	26
		23
Lockett 140, completely mercerized without tension	[a] .2	100

[a] As 2- to 3-g samples were used for these measurements, the values obtained are regarded as approximate.

TABLE 8. *Effect of reduction in crystallinity by amine treatment on specific surface of cotton yarn*

Yarn	Crystallinity [a]	Specific surface of unswollen yarn [b]	Specific surface after swelling in water, followed by solvent exchange and drying
	Percent	m^2/g	m^2/g
Co-3647, control yarn	90.8± 1.6	0.2	21
		.5	18
Co-3978, prepared from above by ethylamine treatment	43.3±10.7	.7	16
		.8	23

[a] Measurements made by C. M. Conrad of the Southern Regional Research Laboratory, U. S. Department of Agriculture.
[b] As 2- to 3-g samples were used for these measurements, the values obtained are regarded as approximate.

TABLE 9. *Effect of treatment with water followed by solvent exchange and drying on specific surface of hydrocellulose*

Sample	Specific surface
	m^2/g
Air-dried	0.7
	.6 (a)
	.7
Solvent exchanged and dried	6
Treated with water, solvent exchanged, and dried	127
	125

[a] As 2- to 8- g samples were used for these measurements, the values obtained are regarded as approximate.

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regions of cellulose by dissolution and recrystallization, it was expected that the specific surface of air-dried hydrocellulose would be greater than that of air-dried cotton but would show no increase when the hydrocellulose was treated with water, subjected to solvent exchange, and dried. Instead, it was found that the specific surface of air-dried hydrocellulose was essentially the same as that of cotton fiber, and on treatment with water, followed by solvent exchange and drying, it increased to 126 m^2/g. In order to determine whether this increase might be the result of the dehydrating action of the solvents used in the exchange process rather than the result of swelling, a sample of the hydrocellulose was subjected to solvent exchange and drying without the usual treatment with water. This resulted in a specific surface of approximately 6 m^2/g, an increase of the magnitude to be expected as the result of removal of the normal regain moisture by solvent exchange. Thus it appears that treatment with water plays an important role in the development of the larger surface area of 126 m^2/g, possibly by separating close-fitting crystallites sufficiently for all or most of their surfaces to be available to nitrogen.[5]

The results of specific-surface measurements on a series of methanolyzed celluloses prepared by reaction of purified cotton with 0.5 molar hydrochloric acid in absolute methanol at 30° C for varying periods of time are given in table 10.[6] They show that the surface available to nitrogen after swelling decreases rapidly during the first few hours of methanolysis and then increases; the products of 5, 50, and 240 hr of methanloysis having specific surfaces approximately ⅛, ¼, and ½ as large, respectively, as that of the purified cotton used in their preparation. Between 240 and 976 hr of methanolysis, little if any further change occurs. This suggests the operation of two forces: one resulting in a reduction in the surface available after swelling, the other in an increase. The former is explicable in terms of the removal of amorphous cellulose by dissolution or recrystallization; the latter by the separation of close-fitting crystallites, upon treatment with water followed by solvent exchange, so that all surfaces are available to nitrogen. That two forces also operate during the hydrolysis of cellulose is suggested by surface areas calculated from water sorption data[7] on hydrocelluloses prepared from cotton and viscose rayon (table 11).

The results of this investigation suggest that nitrogen-sorption measurements on swollen cottons may be used in evaluating the effect of various treatments on cottons and other cellulose fibers. In interpreting these measurements, however, it must be borne in mind that some collapse of the expanded cellulose undoubtedly occurs during the exchange and drying procedure with the result that the specific surfaces of these samples are not those of completely swollen cottons. How great the collapse is, or to what extent it is responsible for the fact that the values obtained for specific surfaces of swollen cottons by the nitrogen method are much smaller than those obtained by other methods (table 12) is yet to be determined.

[5] Nelson [19] found that hydrocellulose was reduced to very fine particles on beating in a Waring blender for only 30 sec. Measurements on electron micrographs of these particles indicated that their surface area was of the same order of magnitude as that of water-treated, solvent-exchanged hydrocellulose.

[6] This series of methanolyzed celluloses is that described by Reeves [20].

[7] These moisture sorption data were obtained at the request of C. M. Conrad of the Southern Regional Research Laboratory for use in another project.

TABLE 10. *Effect of methanolysis on specific surface of cotton cellulose*

Methanolysis carried out at 30° C in 0.5-*M* HCl in absolute methanol.

Sample	Specific surface of unswollen cellulose [a]	Specific surface after treatment with water followed by solvent exchange and drying
	m^2/g	m^2/g
1. Purified Empire cotton	.....	28 24
2. Prepared from 1 by methanolysis for 1 hr	0.4 .7	20 17
3. Prepared from 1 by methanolysis for 5 hr	.....	9
4. Prepared from 1 by methanolysis for 50 hr	.....	6 7
5. Prepared from 1 by methanolysis for 240 hr	.....	11 16
6. Prepared from 1 by methanolysis for 600 hr	.....	16 20
7. Prepared from 1 by methanolysis for 976 hr	1.6 1.9	16 14

[a] As 3-g samples were used for these measurements, the values obtained are regarded as approximate.

TABLE 11. *Effect of hydrolysis on specific surface of cotton and viscose rayon*

Sample	Specific Surface [a]
	m^2/g
Co-4152, cotton	114
Co-4153, prepared from Co-4152 by hydrolysis for 20 min	84
Co-4154, prepared from Co-4152 by hydrolysis for 7 hr	95
Co-4155, viscose rayon	193
Co-4156, prepared from Co-4155 by hydrolysis for 6 min	130
Co-4157, prepared from Co-4155 by hydrolysis for 1.5 hr	145

[a] Specific surfaces calculated from adsorption of water at 35° C, using the Brunauer, Emmett, and Teller equation.

TABLE 12. *Specific surface of swollen cotton as determined by methods other than low-temperature nitrogen sorption*

Sample	Method	Specific surface	Reference
		m^2/g	
Purified cotton linters, swollen in 10% NaOH, washed, solvent exchanged and dried.	Thallous ethylate	170 330 420 520	[3]
Purified cotton (swollen by adsorbate).	Water vapor sorption	108	[21]
Do	do	220	[22]
Do	Sulfur dioxide sorption	130	[22]
Do	Ammonia gas sorption	200	[22]
Do	Hydrogen chloride gas sorption.	90	[22]
Purified cotton	Heat of swelling and adhesion tension of water.	140	[22]

4. Summary

1. Unswollen cotton fibers differing in variety, maturity, and previous history showed relatively small differences in surface area as measured by the method of Brunauer, Emmett, and Teller; the surface area in all cases being less than 1 m^2/g.

2. Cotton fibers that had been swollen in water, then dehydrated by a process of solvent exchange, and dried under anhydrous conditions were found to have surface areas many times those of the unswollen fibers.

3. Studies on an absorbent cotton showed the increase in surface to be dependent on time and temperature of swelling.

4. When swollen and dehydrated under the same conditions, cottons differing in previous history had surface areas ranging from 4 to 148 m^2/g. Purification and mercerization produced increases in the surface available after swelling; methylenation produced a decrease; ethylamine treatment had no effect.

5. Studies on a series of methanolyzed cottons suggested the operation of two forces during methanolysis, one resulting in a decrease in the surface available after swelling, the other in an increase.

6. The correlation of the nitrogen method with other methods used for determining the specific surface of swollen cellulose requires further study.

The authors express their appreciation to John W. Rowen for suggesting this investigation and to John R. Gustafson, Jr., Charles K. Mann, and Walter K. Stone for technical assistance.

5. References

[1] C. M. Hunt, R. L. Blaine, and J. W. Rowen, J. Research NBS **43,** 547 (1949) RP2048.
[2] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. **60,** 309 (1938).
[3] A. G. Assaf, R. H. Haas, and C. B. Purves, J. Am. Chem. Soc. **66,** 59 (1944).
[4] A. G. Assaf, R. H. Haas, and C. B. Purves, J. Am. Chem. Soc. **66,** 66 (1944).
[5] P. H. Emmett, A new method for measuring the surface areas of finely divided materials and for determining the size of particles. Symposium on new methods for particle size determinations in the subsieve range, p. 95–105 (American Society for Testing Materials, Philadelphia, Pa., 1941).
[6] W. E. Barr and V. J. Anhorn, Scientific and industrial glassblowing, p. 271 (Instruments Publishing Co., Pittsburgh 12, Pa., 1949).
[7] S. Brunauer, The adsorption of gases and vapors, p. 155 (Princeton University Press, Princeton, N. J., 1945).
[8] S. S. Kistler, J. Phys. Chem. **36,** 52 (1932).
[9] K. L. Hertel and C. J. Craven, Textile Research J. **21,** 765 (1951).
[10] I. Gailey, J. Soc. Dyers & Colourists **67,** 357 (1951).
[11] C. F. Goldthwait, Textile Research J. **21,** 55 (1951).
[12] R. E. Wagner and E. Pacsu, Textile Research J. **22,** 12 (1952).
[13] A. R. Urquhart and A. M. Williams, Shirley Institute Mem. **4,** 5 (1925); J. Textile Institute **16,** T155 (1925).
[14] A. R. Urquhart and A. M. Williams, Shirley Institute Mem. **5,** 303 (1926); J. Textile Institute **18,** T55 (1927).
[15] S. M. Neale, J. Textile Institute **22,** T320, T349 (1931).
[16] E. Knecht, J. Soc. Dyers & Colourists **24,** 68, 107 (1908).
[17] P. H. Hermans, Physics and chemistry of cellulose fibers, p. 41 (Elsevier Publishing Co., Amsterdam, 1949).
[18] L. Segal, M. L. Nelson, and C. M. Conrad, J. Phys. Chem. **55,** 325 (1951).
[19] M. L. Nelson, Southern Regional Research Laboratory of the U. S. Department of Agriculture. Private Communication.
[20] R. E. Reeves, L. W. Mazzeno, and C. L. Hoffpauir, J. Am. Chem. Soc. **72,** 4773 (1950).
[21] J. W. Rowen and R. L. Blaine, J. Research NBS **39,** 479 (1947) RP1842.
[22] A. J. Stamm and M. A. Millett, J. Phys. Chem. **45,** 43 (1941).

WASHINGTON, July 10, 1952.

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Measurement of Multimegohm Resistors

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The method by which multimegohm resistors are measured at the National Bureau of Standards is a null method using an electrometer as the null detector. The charge flowing through the resistor during the time of measurement is obtained from a variable air capacitor maintained at a fixed potential. The potentials across the variable air capacitor and thus across the specimen are maintained constant as indicated by the null reading of the electrometer by decreasing the capacitance of the air capacitor at just the right rate. The capacitance of the capacitor is varied by a small direct-current motor geared to the shaft of the capacitor and whose speed can be controlled. Several multimegohm resistors of two different makes have been studied over a period of about three years. Although these are the most stable multimegohm resistors available, it was found that they had erratic fluctuations of 0.5 to 1 percent and were generally voltage sensitive. With the impressed voltage varied from 1.5 to 180 volts, various resistors showed resistance changes ranging from 0.4 to 26.9 percent.

1. Introduction

This paper has been prepared in response to numerous requests for a description of the methods used in the National Bureau of Standards for calibrating resistors having values above those conveniently and economically available in wire-wound form. A practical limit for wire-wound resistors may be taken as 10^7 ohms.

Bridges equipped with suitable detectors and capable of being balanced with a precision of a few tenths of a percent are commercially available for measurements in the range 10^7 to 10^{13} ohms. All of these equipments are comparison devices and involve the use of standard resistors either directly as components in the bridge circuit or as auxiliary calibrating units to be used in place of the unknown resistor. It is an unfortunate fact that even the best multimegohm resistors produced today do not possess sufficient stability to serve as reliable standards in the range mentioned above. A later section of this paper will present the results of a 3-year study in this Bureau on the best obtainable multimegohm resistors.

In the absence of suitable standards in this range, resistors must be evaluated by the application of other principles of measurement. These usually involve a variation of either the charge accumulation or the loss-of-charge method. For either method the null detector is usually an electrometer. In the accumulation method [1] [2] [3] the charge flowing through the resistor is accumulated on a capacitor having good insulation. The potential from one side of the capacitor to ground is continuously increased at a rate such that the potential across the resistor remains the same throughout the measurement as indicated by the electrometer. The total charge that flows through the resistor in a known time is obtained from a knowledge of the capacitance of the capacitor system and the potential to which the capacitor becomes charged as indicated by the potentiometer. The disadvantages of this method are the difficulty of accurately determining the effective capacitance and the difficulty of procuring a continuously variable potentiometer having the range and precision of setting desired.

A method for measuring small currents described by P. J. Higgs [4] uses a variable capacitor rather than a potentiometer to measure the charge that flows through the resistor. In this case the loss-of-charge method is used. The charge that flows through the resistor is supplied by the variable air capacitor. Constant potential across the resistor as indicated by the electrometer is obtained by continuously decreasing the capacitance at the proper rate. It is not necessary to know the total capacitance of the system, only the amount by which the capacitance has been changed during measurement.

2. Method of Measurement

A slightly modified version of the Higgs' method has been developed by the present author. A diagram of the circuit is shown in figure 1. A potential divider is used to provide the potentials for the specimen and variable air capacitor rather than direct battery connections. This permits the ratio of the voltages to be more easily determined with the desired accuracy than when the voltages are measured. A small d-c motor is geared to the shaft of the variable air capacitor so that the capacitance can be changed more smoothly than by hand.

The basic principle of this method may be understood from the following considerations: Before the start of a measurement the switch, s, across the detector is closed; the capacitor, C_x, is charged to the full voltage of the battery, V; and a steady current of magnitude $i=(r_x/r_z)(V/X)$ is flowing through the unknown resistor, X, the latter being very large compared with r_x. At time $t=0$ switch s is opened, and, if no other adjustments were made, the capacitor discharges exponentially to some lower voltage of

[1] John S. Townsend, The genesis of ions by the motion of positive ions in a gas, and a theory of the sparking potential, Phil. Mag. 6, 598 (1903).
[2] L. S. Taylor, Accurate measurement of small electric charges by a null method, BS J. Research 6, 807 (1931) RP306.
[3] H. H. Race, Electrical conduction in hard rubber, Pyrex, quartz, and crystalline quartz, Trans. AIEE 47, 1044 (1928).
[4] P. J. Higgs, A method of measuring high insulation resistance, J. Sci. Instr. 10 169 (June 1933).

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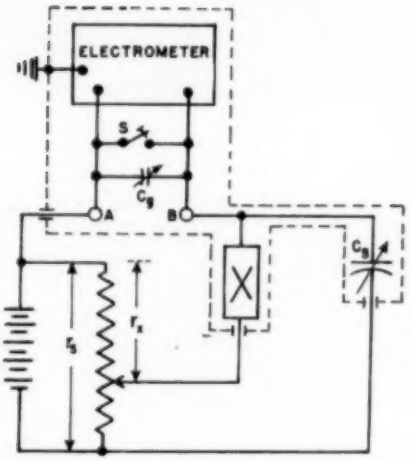

FIGURE 1. *Circuit used to measure multimegohm resistors.*

magnitude dependent upon the setting of the contact P. The procedure is to decrease the value of C_s continuously and smoothly in such a manner that the potential difference across it remains constant at its initial value as its charge diminishes. The rate at which C_s is decreased is such that the potential difference across open switch s remains zero as indicated by the detector. It will be obvious, therefore, that current through X is being maintained constant at its initial value i, with the difference that the energy dissipated in X is now furnished by the capacitor rather than the battery. Under these conditions the pertinent equation is:

$$R = \frac{V_x}{V_s}\frac{\Delta t}{\Delta C}, \tag{1}$$

where R is the resistance of the specimen, ΔC is the change in capacitance during time interval Δt and V_x and V_s are the potentials across the specimen and variable air capacitor, respectively. Since the current through the specimen is negligibly small compared to the current in the potential divider, the ratio V_x/V_s may be taken equal to r_x/r_s and eq (1) becomes:

$$R = \frac{r_x}{r_s}\frac{\Delta t}{\Delta C}. \tag{2}$$

3. Description of Equipment

Any good electrometer having the required sensitivity may be used as the null instrument to indicate when points A and B of figure 1 are at the same potential. The insulation between the terminals of the electrometer must be of such quality that the leakage current will be negligible compared to the current flowing through the specimen. Two types of electrometers have been used, a Compton quadrant electrometer and a vibrating-reed electrometer.[5] The equipment used in the latter case is shown in figure 2.

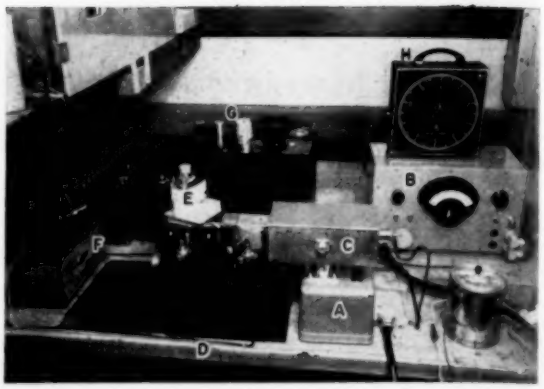

FIGURE 2. *Equipment used to measure multimegohm resistances when the vibrating-reed electrometer is the null indicating instrument.*

A, Electrometer head; B, electrometer controls; C, specimen shield; D, variable air capacitor, C_s; E, motor drive for variable air capacitor; F, voltage divider; G, variable capacitor, C_g.

When the Compton quadrant electrometer is used, the point A is directly connected to ground. The quadrant electrometer has a sensitivity such that a potential of 1 mv produces a deflection of about 1.5 mm at a scale distance of 2 m. Its period is about 11 sec, and this relatively long interval is a serious disadvantage when trying to observe potential changes and to compensate for them.

Of the two, the vibrating-reed electrometer is both more sensitive and more rapid in its response. Its sensitivity is such that a potential of 1 mv produces a meter deflection of 50 scale divisions. The response is almost instantaneous. A disadvantage is that neither of the measuring terminals may be connected to ground. This requires that all equipment be insulated from ground. Another disadvantage is that on the most sensitive range it has a zero drift that must be determined and for which a correction must be applied. The vibrating-reed electrometer is, however, generally more satisfactory than the quadrant electrometer.

The capacitor, C_s, must have negligible leakage between its plates. A three-terminal variable air capacitor is used. Each set of plates is insulated from the frame and case. There is no dielectric directly between the plates. Conductance to ground on the high-potential side causes no error because the leakage current returns to the battery without affecting the electrometer. There is no difficulty in keeping the leakage to ground on the low side sufficiently low because this part of the circuit is maintained at, or near, zero potential at all times, and the leakage current is therefore negligible.

[5] This electrometer converts a d-c potential into an a-c potential by means of a reed vibrating near an anvil on which the d-c potential appears. The a-c potential is then amplified and rectified. A negative feedback stabilizes the circuit. A full description of this type of electrometer is given by H. Palevsky, R. K. Swank, and R. Grenchik, Design of dynamic condenser electrometers, Rev. Sci. Instr. 18, 298-314 (May 1947).

It has been found that when the relative humidity rises above about 40 percent appreciable conduction does occur directly between the plates of the capacitor. This is probably due to very fine fibers that are generally floating in the air and which settle onto the plates, occasionally bridging them. When a drying agent is placed in the capacitor, this conductance disappears.

Any one of three capacitors having ranges of 9.5 to 20.5, 15 to 125, and 100 to 1,100 picofarads (micromicrofarads) are available for use in the measurements of resistance. With these capacitors, and with proper potentials applied to them, measurements can be made involving currents from 10^{-9} to 10^{-13} amp. For instance, if a 10^9-ohm resistor is being measured at 1.5 v, it will be seen from eq (1) that a potential of 500 v will be required on the variable air capacitator for a capacitance change of 900 picofarads in 300 sec. If a 10^{13}-ohm resistor is being measured at 1.5 v, a potential of 15 v will be required on the variable air capacitor for a capacitance change of 9 picofarads in 900 sec.

It is necessary to decrease the capacitance of the capacitor, C_s, at a specific uniform rate. For this purpose, a small d-c motor is geared to the shaft of the capacitor, as shown in figure 3. When using the vibrating-reed electrometer, the motor must be insulated from the shaft and frame of the capacitor, so a fiber gear and insulating supports are used. The speed of the motor is controlled by a series resistance. This resistance is adjusted so that the speed of the motor is just below the proper speed, and small changes in the speed are made by shorting part of the resistance by means of a key. By closing this key momentarily with varying regularity, it is possible to keep the potential between points A and B within plus or minus 1 mv as indicated by the electrometer.

The potential divider is a plug box having a total resistance of 1 megohm. This resistance is low compared to the resistances being measured, and yet is high enough to prevent undue drain on the battery used for potential source. The potential source must be very steady. The voltage on the variable air capacitor must not change sufficiently during the period of measurement to cause a change of charge on the capacitor, which is appreciable compared with the total charge that flows through the specimen. The charge Q_x that flows through the specimen during measurement is given by $Q_x = V_s \cdot \Delta C$, and the charge change due to voltage change is given by $Q_s = C \cdot \Delta V$. If the ratio Q_s/Q_x is to be less than the limit of error L, then ΔV must be less than $L(\Delta C/C)V_s$. If the limit of desired error is 0.1 percent, ΔC is 9 picofarads, and C is 20 picofarads, then ΔV must not be more than 0.045 percent of V_s. It has been found that heavy-duty radio B batteries will satisfy this requirement when connected to a potential divider that causes a current drain not exceeding 0.5 ma.

The time is measured by means of an electric timer that indicates to tenths of a second. This timer is started by a switching mechanism that opens switch S and starts the motor driving the capacitor C_s so that all three events occur simultaneously.

FIGURE 3. *Motor drive for variable air capacitor*

For attainment of the desired accuracy (limit of error of 0.1 percent in the present case), the following requirements must be met. (1) The capacitance change, ΔC, during measurement must be large enough so that it can be determined with the required accuracy. This depends upon the range of the capacitor being used. (2) The time of measurement must be long enough so that Δt can be determined with the required accuracy. The timer used in this work can be read to 0.1 sec, so a time of measurement of about 300 sec is generally used. (3) The sensitivity of the electrometer to voltage must be such that in combination with proper regulation, the deviations of the potential between points A and B from zero are negligible in comparison to the voltage applied to the specimen.

4. Measurement Procedure

The measurement procedure can be best described by an example such as the following. Suppose that a resistor having a nominal value of 10^{10} ohms is to be measured at 1.5 v. A time of measurement of 300 sec is chosen. If the capacitor having a range of 1,000 picofarads is used, a ΔC of 900 picofarads is chosen. As seen from eq (1), choice of the above three values will require that the voltage on the capacitor be 50 v. As this is also the value of the voltage across the voltage divider, the battery connections are adjusted to give that value as nearly as possible. The battery pack is so constructed that its voltage output can be adjusted in steps of 1.5 v. As 0.5 ma is the current chosen for the potential divider, the resistance of the potential divider is adjusted to 100,000 ohms. The tap for the specimen is placed at 3,000 ohms to give 1.5 v. The value of the voltage across the potential divider is watched by means of a potentiometer connected across 300

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ohms. To keep the sensitivity of the circuit within a practical working range, the value of C_g is adjusted until the potential difference across the open switch, s, changes at the rate of about 20 mv/sec when the capacitance, C, remains fixed. An appreciably higher rate than this makes it difficult to adjust the speed of the driving motor on the variable air capacitor quickly enough to keep the potential difference across the open switch, S, from fluctuating more than 1 mv. The equipment is now adjusted for measurement.

To make a measurement, switch s is closed, the capacitor is set at its highest value, and the battery is connected to the potential divider. At time $t=0$, switch s is opened at the same time that a switch is closed, which starts both the motor drive on the capacitor and the timer. The potential difference across the open switch, s, is kept less than 1 mv (with practice it can be kept less than 0.4 mv) by slightly changing the speed of the driving motor. At the end of about 300 sec the switch is opened, which stops the motor and timer. Switch s is then closed. The capacitance difference is determined from its original and final readings, and the time interval is read from the timer. The resistance of the specimen is computed by eq (2). The capacitor is then reset to its highest value, the timer reset to zero, the battery to the potential divider is reversed, and another measurement is made, as described above. An average of this pair of measurements is considered a single determination. Two determinations are made on each specimen.

5. Accuracy and Precautions

A limit of error of 0.1 percent can be obtained with this equipment if the following precautions are observed. The capacitance difference, ΔC, should be large enough so that it can be determined with the required accuracy. The variable air capacitors used are calibrated to 0.01 percent of their maximum range. Because only about nine-tenths of the maximum range is used in a measurement and inaccuracies due to stopping the motor are involved, ΔC cannot be determined with an accuracy greater than about 0.04 percent.

The time interval, Δt, must be of such duration that it can be determined with sufficient accuracy. Because the timer reads to 0.1 sec, 300 sec is chosen. Care must be taken to assure that the timer is started at the same instant switch s is opened. Under present procedure, the error due to lack of the synchronization is not greater than 0.1 sec. Thus Δt can be determined with an accuracy of 0.03 percent.

The resistances in the potential divider can be readily determined to 0.01 percent, so these present no problem regarding limit of error.

It is not possible to keep the potential difference across the open switch, s, always at zero. The appearance of this potential causes an error in two ways. It changes the potential across the specimen and across the capacitor. Because a voltage of 1.5 v is applied to the specimen, a voltage of 0.5 mv across switch, s, would change the voltage on the specimen and hence the current by about 0.03 percent. The potential that appears across the switch, s, is random in nature, being both positive and negative, so the average effect is less than 0.03 percent.

The appearance of a potential across switch s also changes the potentials across the capacitors, C_s and C_g. The appearance and disappearance of these random potentials do not affect the measurement except as they produce a leakage of charge over the insulation from the low-potential side of the capacitor, C_s, to the shield or through the insulation of the capacitor, C_g. If the insulation is good (10^{10} ohms or greater), this leakage will be neglibible. However, if the measurement is terminated at a time when the potential across the switch s is a maximum of 0.5 mv, then the resistance of the specimen as computed by eq (2) will be in error because part of the charge that flowed through the specimen came from a change in potential of the capacitors, C_s and C_g, rather than from a change in capacitance of capacitor C_s. The error due to this can be estimated by recalling that C_g is adjusted so that the rate of change of potential across switch s is about 20 mv/sec when the capacitance, C_s, remains fixed. This is equivalent to about 6,000 mv in the 300 sec during which the measurement is made, so an error of 0.5 mv at the end of the measurement would cause an error of about 0.01 percent.

In those cases where the current flow is less than 10^{-12} amp (resistance greater than 10^{12} ohms at 1.5 v), the capacitance desired for C_g becomes less than the minimum capacitance of the system and cannot be realized. Therefore, the measurement time must be increased correspondingly if the same acurracy is to be obtained.

Because of the small currents involved, it was found necessary to take special precautions in shielding to eliminate spurious effects. It was found that contact-potential differences of different metals in the shielding and conductor can cause a drift of the electrometer even though no potential is applied. It was not practical to make all parts of the equipment from the same metal. However, the effect was virtually eliminated by the proper selection by a cut-and-try process of metals for the various parts. Correction for the residual can be made by making measurements with the battery connected direct and reversed. An average of these two measurements gives a value from which the error is eliminated, provided the effect does not change during the time of measurement. The terminals on some of the resistors are especially bad in this respect. The trouble from specimen terminals may be eliminated by surrounding the terminal with a sheath of metal that does not produce a drift of the electrometer. A bare copper wire wound into a tight helix makes an excellent sheath.

There is a drift in the vibrating-reed electrometer that is equivalent to a current of about 10^{-16} amp. This is not significant when measuring resistances below 10^{12} ohms, but becomes appreciable for

resistances above this value. This drift is sufficiently constant over the period of measurement, so that an average of two measurements with reversed battery practically eliminates this effect.

To test the equipment for spurious currents, a measurement is made with the resistor removed from the circuit. When the circuit is set for measuring resistances in the range 10^9 up to 10^{11} ohms, and when it is operating properly, no detectable change in potential (equivalent to less than 0.02 percent of the resistance for which the circuit is set to measure) is observed across open switch s in 300 sec. When the circuit is set for measuring resistances of the order of 10^{13} ohms, the readings are appreciable and somewhat erratic. The potential appearing across open switch s always has the same polarity, regardless of the polarity of the battery across the potential divider and is great enough to produce an error of from 0.1 to 0.5 percent. Averaging a pair of measurements with the battery reversed tends to cancel this effect, but because this effect is somewhat erratic, the limit of error for measurements of 10^{13} ohms is 0.2 to 0.3 percent.

6. Aging and Voltage Coefficient of Certain Commercial Resistors

A number of multimegohm resistors have been studied over the past 3 years, during which time they have been kept under standard laboratory conditions (23° C and less then 50 percent relative humidity). Most of these resistors have been measured by the method described in this paper, but a few of these resistors had resistances too low to be measured in this manner. These latter resistors were measured either by the "comparison method, using a galvanometer" described in ASTM Tentative methods of test for electrical resistance of insulating materials D257–52T, or more lately by means of the Wheatstone bridge. The study included two types of resistors. One type (1.2–1 through 1.2–9) consisted of a small coated rod sealed in a glass envelope. The glass envelope had been treated to reduce surface conductance. The other type (1.2–10 through 1.2–14) consisted of molded composition material.

The values of resistance fluctuated with time, as shown in figure 4 and were a function of the voltage

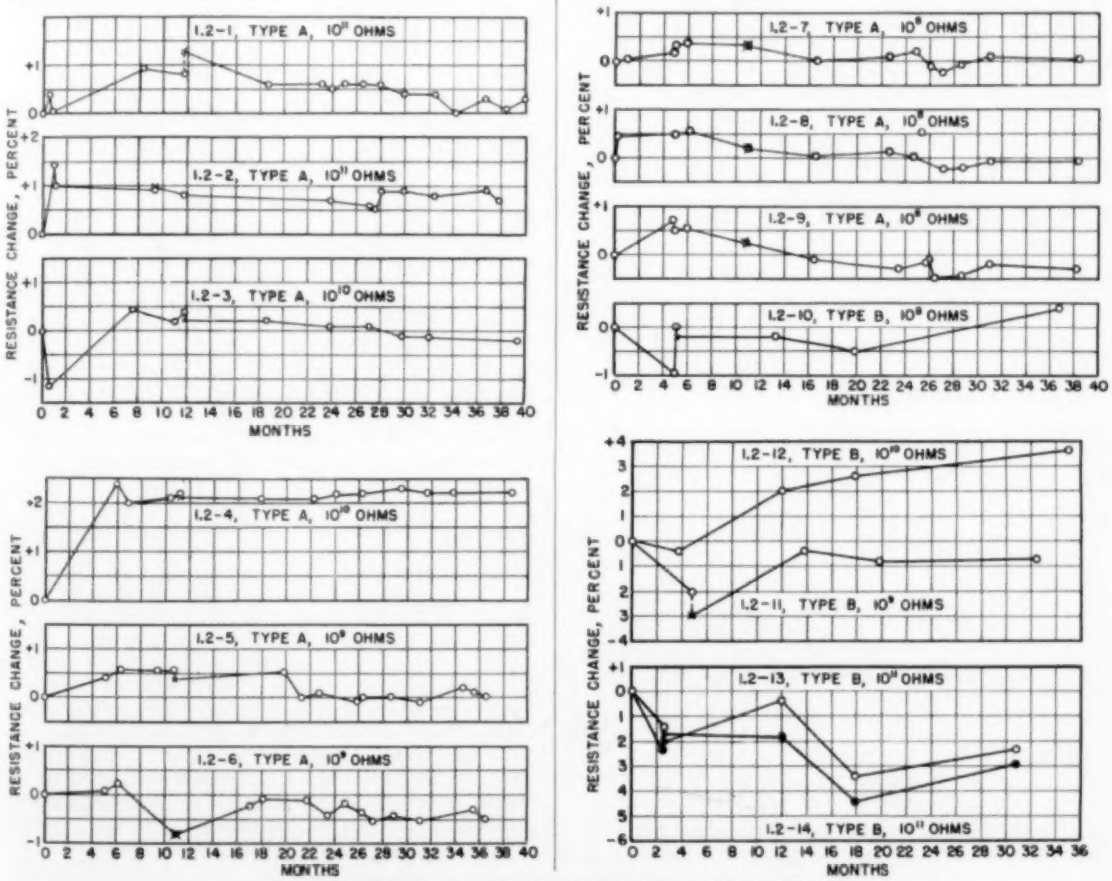
1.2-1, TYPE A, 10¹² OHMS
1.2-2, TYPE A, 10¹¹ OHMS
1.2-3, TYPE A, 10¹⁰ OHMS
1.2-4, TYPE A, 10⁹ OHMS
1.2-5, TYPE A, 10⁹ OHMS
1.2-6, TYPE A, 10⁹ OHMS
1.2-7, TYPE A, 10⁹ OHMS
1.2-8, TYPE A, 10⁹ OHMS
1.2-9, TYPE A, 10⁹ OHMS
1.2-10, TYPE B, 10⁹ OHMS
1.2-12, TYPE B, 10¹⁰ OHMS
1.2-11, TYPE B, 10⁹ OHMS
1.2-13, TYPE B, 10¹² OHMS
1.2-14, TYPE B, 10¹¹ OHMS
RESISTANCE CHANGE, PERCENT
MONTHS

FIGURE 4. *Change of resistance of multimegohm resistors with time.*
The crosses are values obtained after the resistors had been subject to a voltage of 180 volts.

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at which they were measured, as shown in table 1. The values of the molded composition resistors (1.2–10 to 1.2–14) fluctuate more with time than do the glass-sealed resistors (1.2–1 to 1.2–9), which may be due to humidity effects. One of the molded composition resistors (1.2–12) now has over twice the resistance that is stamped on it. When originally received about 12 years ago, it was measured by a moderately accurate method (limit of error probably about 2 percent) and found to have approximately the value of resistance stamped on it. This means that in the intervening years, the resistance had doubled. This is the resistor that shows the greatest voltage coefficient.

Three other types of resistors have been tested, but their stability was so much poorer than the two mentioned above that no extended study has been made of them.

There is some indication that the fluctuations in resistance of some of the sealed resistors are decreasing with age. But even the best of these resistors have erratic fluctuations of resistance of the order of 0.5 percent.

The effect of change in voltage is often very different for different resistors, even when they are the same make (see table 1). The percentage changes between 1.5- and 180-v range from 0.4 to 26.9 percent. There appears to be no significant difference between the two types of resistors as regards effect of voltage.

Although the null-electrometer method described above is capable of measuring resistances up to 10^{12} ohms at 1.5 v, with a limit of error of 0.1 percent, no multimegohm resistors (10^9 ohms or above) have been noted that are stable with time to that accuracy. They all have voltage coefficients. All these things considered, the presently available resistors may not be relied upon to maintain their values closer than 0.5 to 1.0 percent. There is great need for a more stable resistor for use as a standard in the multimegohm range.

TABLE 1. *Change of resistance of multimegohm resistors with voltages above 1.5 volts*

Resistor	Volts		Nominal value
	1.5 to 45	1.5 to 180	
	%	%	*Ohms*
1.2–1	−2.0	−8.3	10^{11}
1.2–2	------	−3.4	10^{11}
1.2–3	−0.4	−2.5	10^{10}
1.2–4	−.4	−2.5	10^{10}
1.2–5	−.4	−2.7	10^{9}
1.2–6	+.7	−1.5	10^{9}
1.2–7	0	−1.9	10^{9}
1.2–8	−.5	−3.0	10^{9}
1.2–9	−3.9	−12.4	10^{9}
1.2–10	−0.1	−1.1	10^{8}
1.2–11	+.6	−0.4	10^{8}
1.2–13	------	−0.4	10^{11}
1.2–14	−0.3	+2.0	10^{11}
1.2–12	−10.4	−26.9	2×10^{12}

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Temperature Dependence of Compression of Natural Rubber-Sulfur Vulcanizates of High Sulfur Content[1]

Charles E. Weir

Measurements are reported of the compression of rubber-sulfur vulcanizates in the temperature range 10° to 81.5° C between pressures 1,000 and 10,000 atmospheres. Sulfur contents varied from 10 to 28 percent. Empirical isothermal compression equations are derived. Empirical isobaric equations are derived for specific volume. From the isobars empirical equations of state (pressure-volume-temperature) are derived.

1. Introduction

In the course of a continuing investigation of the behavior of high-polymeric materials under high pressures, measurements have been made on the pressure-volume-temperature (PVT) relationships of natural rubber-sulfur vulcanizates. This report is concerned with the experimental data obtained on these vulcanizates between 10° and 81° C and between 1,000 and 10,000 atm. Empirical equations have been derived to fit the data.

These data will be used later to obtain a clear answer to the question of the effect of pressure on the second-order or glass transition in polymers and also to evaluate thermodynamic quantities that may prove of interest in correlating molecular or intrachain forces in such polymers. The discussion and calculations involved in these two objectives are deferred for subsequent reports, inasmuch as the compilations of the compression data and the derived equations are quite lengthy. However, the data given here are sufficient for all projected treatment of these objectives.

The behavior of rubber under pressure has been studied by Adams and Gibson [1],[2] Bridgman [2], Scott [3], and the present author [4]. All previous work except that of Scott [3] was carried out at room temperature and high pressure. The studies of Adams and Gibson, and of Bridgman were conducted on available rubbers of uncontrolled composition, whereas those of reference 4 were carried out on raw, synthetic, and oil-resistant rubbers. Scott [3] worked only in the low-pressure range (maximum 800 bars) but systematically varied composition (sulfur content) and temperature over a wide range. These data of Scott have received a great deal of consideration by current workers in the high-polymer field because they are the only available PVT data on rubbers of various sulfur contents. From consideration of the data presented graphically and in empirical equations by Scott, it would appear that certain questionable conclusions concerning the effect of pressure on the glass transition of rubbers have been drawn by later workers from these data. It must be recalled that the significance of the discontinuities in slopes observed by Scott in the isobars was not known at the time the measurements were made and the numerical experimental data were not reported. The present report is designed to supplement the previous studies of Scott.

2. Preparation and Treatment of Specimens

The rubber specimens used were prepared from smoked sheet and sulfur and contained no filler. Sulfur was incorporated in the milling operation and the resulting mixture molded into cylinders approximately $\frac{1}{2}$ in. in diameter and 4 in. in length Vulcanization was carried out at 140° C for 17 hr to insure combination of the sulfur with the rubber. Sulfur contents reported refer to amounts added because chemical analyses have not been performed. However, as the densities of these specimens agree well with the densities of specimens of corresponding sulfur content reported by Scott, it is considered that practically all the sulfur combined with the rubber. Specimens were prepared to contain sulfur contents between 10 and 28 percent, the use of rubbers of lower sulfur contents being considered impractical in these experiments because of the swelling action of the confining liquid on the rubber.

Prior to each experiment at 21° C, the weight of each specimen was determined in air, and immediately following compression it was redetermined in the confining liquid—a light petroleum distillate—and in air. The former two weights permitted calculation of the volume and density of the specimen, whereas the latter weight permitted estimation of the quantity of liquid absorbed in the experiment. Densities were determined only at 21° C, but initial and final weighings in air at 21° C were carried out when specimens were run at elevated and reduced temperatures. The quantities of confining liquid absorbed increased with increasing temperature but in no instance reached a magnitude sufficient to cause doubt as to the validity of the experimental data.

3. Experimental Method

The apparatus and experimental details have been described in detail previously [5]. An experiment consists in forcing a leak-proof piston into the bore of a heavy-walled cylinder that contains the specimen

[1] This paper is a preliminary summary of work on a project sponsored by the Office of Naval Research project NR 330-032.
[2] Figures in brackets indicate the literature references at the end of this paper.

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and a manganin pressure gage immersed in a light petroleum distillate. Measurements of the depth of penetration of the piston are made at every 1,000 atm. Combination of these measurements with similar data obtained in an experiment in which the specimen is replaced by a steel bar of comparable volume permits calculation of the compression, $-\Delta V/V_0$, of the specimen in terms of that of steel, which is known [6]. This compression is reckoned from the arbitrary reference pressure of 2,000 atm but is calculated in terms of the initial (1 atm) volume of the specimen, V_0.

At elevated or reduced temperatures the entire hydraulic press and pressure vessel were enclosed in a thermostatted container so designed as to minimize the possibility of setting up thermal gradients in the pressure vessel. Because air was used as the heat-exchange medium and the heat capacity of the press and pressure equipment was enormous, at least 48 hr was required for attainment of temperature equilibrium after every change of temperature. Temperatures were measured with a calibrated mercury thermometer set in a well in a massive brass block fastened to and in intimate thermal contact with the pressure vessel. This block was also used to contain the temperature compensating manganin coil [5]. During the course of the measurements a maximum temperature variation of ± 0.35 deg C was observed on this thermometer. The enormous heat capacity of the pressure vessel, however, should reduce the temperature variation of the specimen considerably below this figure.

4. Results of Compression Measurements

The results of compression measurements of rubber-sulfur vulcanizates at the various temperatures are given in tables 1 to 6, inclusive. The

TABLE 1. *Compression of natural rubber-sulfur vulcanizates at 10.0° C*

$-\Delta V/V_0$

Pressure	10% S V_0=18.861 cm³ V''=17.918 cm³	13% S V_0=19.117 cm³ V''=18.352 cm³	16% S V_0=17.976 cm³ V''=17.275 cm³	20% S V_0=18.152 cm³ V''=17.482 cm³	
				Run 1	Run 2
atm					
10,000	0.0843	0.0818	0.0834	0.0839	0.0843
9,000	.0758	.0742	.0760	.0759	.0763
8,000	.0686	.0668	.0684	.0683	.0689
7,000	.0616	.0597	.0614	.0618	.0617
6,000	.0531	.0512	.0523	.0530	.0532
5,000	.0427	.0407	.0414	.0420	.0421
4,000	.0315	.0291	.0295	.0297	.0297
3,000	.0182	.0160	.0163	.0157	.0158
2,000	.0000	.0000	.0000	.0000	.0000
1,000	−.0250	−.0214	−.0190	−.0184	−.0186

TABLE 2. *Compression of natural rubber-sulfur vulcanizates at 21.0° C*

$-\Delta V/V_0$

Pressure	10% S V_0=19.000 cm³ V''=18.031 cm³ ρ=0.9947 g/cm³	13% S V_0=19.262 cm³ V''=18.453 cm³ ρ=1.0221 g/cm³	16% S Run 1 V_0=18.141 cm³ V''=17.415 cm³ ρ=1.0518 g/cm³	16% S Run 2 V_0=18.141 cm³ V''=17.434 cm³ ρ=1.0518 g/cm³	18% S V_0=18.586 cm³ V''=17.906 cm³ ρ=1.0707 g/cm³
atm					
10,000	0.0881	0.0864	0.0864	0.0853	0.0868
9,000	.0808	.0790	.0789	.0776	.0781
8,000	.0730	.0710	.0705	.0702	.0715
7,000	.0645	.0624	.0616	.0608	.0624
6,000	.0555	.0531	.0514	.0515	.0525
5,000	.0452	.0425	.0408	.0404	.0416
4,000	.0337	.0311	.0291	.0286	.0292
3,000	.0193	.0173	.0156	.0152	.0160
2,000	.0000	.0000	.0000	.0000	.0000
1,000	−.0255	−.0248	−.0201	−.0194	−.0186

Pressure	20% S Run 1 V_0=18.217 cm³ V''=17.543 cm³ ρ=1.0877 g/cm³	20% S Run 2 V_0=18.217 cm³ V''=17.561 cm³ ρ=1.0877 g/cm³	22% S V_0=18.541 cm³ V''=17.874 cm³ ρ=1.0996 g/cm³	23% S V_0=18.169 cm³ V''=17.515 cm³ ρ=1.1214 g/cm³	28% S V_0=18.633 cm³ V''=17.981 cm³ ρ=1.1422 g/cm³
10,000	0.0878	0.0871	0.0876	0.0892	0.0891
9,000	.0801	.0794	.0801	.0803	.0816
8,000	.0722	.0718	.0722	.0737	.0734
7,000	.0631	.0625	.0628	.0647	.0646
6,000	.0530	.0528	.0532	.0547	.0545
5,000	.0417	.0415	.0419	.0435	.0434
4,000	.0293	.0291	.0298	.0310	.0312
3,000	.0158	.0155	.0156	.0167	.0170
2,000	.0000	.0000	.0000	.0000	.0000
1,000	−.0184	−.0182	−.0184	−.0193	−.0177

BLE 3. *Compression of natural rubber-sulfur vulcanizates at 38.5° C*

$-\Delta V/V_0$

Pressure	10% S $V_0 = 19.238\ cm^3$ $V'' = 18.161\ cm^3$	13% S $V_0 = 19.432\ cm^3$ $V'' = 18.383\ cm^3$	16% S $V_0 = 18.396\ cm^3$ $V'' = 17.642\ cm^3$	18% S $V_0 = 18.706\ cm^3$ $V'' = 17.920\ cm^3$
atm				
10,000	0.0943	0.0896	0.0886	0.0888
9,000	.0871	.0823	.0809	.0810
8,000	.0795	.0746	.0728	.0727
7,000	.0708	.0658	.0633	.0636
6,000	.0617	.0566	.0536	.0537
5,000	.0510	.0462	.0427	.0425
4,000	.0379	.0341	.0307	.0303
3,000	.0211	.0196	.0169	.0164
2,000	.0000	.0000	.0000	.0000
1,000	−.0274	−.0265	−.0240	−.0214
	20% S $V_0 = 18.309\ cm^3$ $V'' = 17.540\ cm^3$	22% S $V_0 = 18.612\ cm^3$ $V'' = 17.898\ cm^3$	25% S $V_0 = 18.216\ cm^3$ $V'' = 17.487\ cm^3$	28% S $V_0 = 18.686\ cm^3$ $V'' = 17.939\ cm^3$
10,000	0.0895	0.0898	0.0908	0.0905
9,000	.0819	.0818	.0831	.0830
8,000	.0734	.0738	.0747	.0748
7,000	.0643	.0652	.0658	.0658
6,000	.0543	.0550	.0558	.0558
5,000	.0431	.0437	.0441	.0445
4,000	.0304	.0309	.0317	.0317
3,000	.0162	.0165	.0165	.0169
2,000	.0000	.0000	.0000	.0000
1,000	−.0205	−.0200	−.0199	−.0197

TABLE 4. *Compression of natural rubber-sulfur vulcanizates at 50.2° C*

$-\Delta V/V_0$

Pressure	10% S $V_0 = 19.370\ cm^3$ $V'' = 18.247\ cm^3$	13% S $V_0 = 19.609\ cm^3$ $V'' = 18.531\ cm^3$	16% S $V_0 = 18.639\ cm^3$ $V'' = 17.689\ cm^3$	18% S $V_0 = 18.786\ cm^3$ $V'' = 17.847\ cm^3$
atm				
10,000	0.0992	0.0932	0.0886	0.0879
9,000	.0912	.0861	.0812	.0802
8,000	.0836	.0780	.0733	.0723
7,000	.0747	.0695	.0643	.0631
6,000	.0650	.0615	.0547	.0533
5,000	.0533	.0496	.0442	.0426
4,000	.0387	.0368	.0321	.0305
3,000	.0212	.0204	.0181	.0167
2,000	.0000	.0000	.0000	.0000
1,000	−.0287	−.0276	−.0264	−.0233
	20% S $V_0 = 18.448\ cm^3$ $V'' = 17.673\ cm^3$	22% S $V_0 = 18.654\ cm^3$ $V'' = 17.889\ cm^3$	25% S $V_0 = 18.297\ cm^3$ $V'' = 17.547\ cm^3$	28% S $V_0 = 18.772\ cm^3$ $V'' = 18.021\ cm^3$
10,000	0.0898	0.0899	0.0910	0.0910
9,000	.0820	.0827	.0835	.0838
8,000	.0734	.0742	.0753	.0753
7,000	.0648	.0648	.0658	.0661
6,000	.0546	.0548	.0554	.0562
5,000	.0433	.0436	.0443	.0445
4,000	.0307	.0309	.0312	.0315
3,000	.0165	.0164	.0167	.0169
2,000	.0000	.0000	.0000	.0000
1,000	−.0213	−.0205	−.0205	−.0210

TABLE 5. *Compression of natural rubber-sulfur vulcanizates at 64.0° C*

$-\Delta V/V_0$

Pressure	10% S $V_0 = 19.522\ cm^3$ $V'' = 18.370\ cm^3$	13% S $V_0 = 19.698\ cm^3$ $V'' = 18.566\ cm^3$	16% S $V_0 = 18.586\ cm^3$ $V'' = 17.581\ cm^3$	18% S $V_0 = 19.005\ cm^3$ $V'' = 18.074\ cm^3$
atm				
10,000	0.1037	0.0972	0.0921	0.0910
9,000	.0956	.0899	.0845	.0832
8,000	.0872	.0822	.0764	.0745
7,000	.0779	.0736	.0673	.0652
6,000	.0675	.0641	.0576	.0554
5,000	.0542	.0527	.0471	.0445
4,000	.0395	.0388	.0346	.0323
3,000	.0217	.0214	.0196	.0180
2,000	.0000	.0000	.0000	.0000
1,000	−.0291	−.0272	−.0271	−.0250
	20% S $V_0 = 18.567\ cm^3$ $V'' = 17.730\ cm^3$	22% S $V_0 = 18.776\ cm^3$ $V'' = 17.989\ cm^3$	25% S $V_0 = 18.318\ cm^3$ $V'' = 17.567\ cm^3$	28% S $V_0 = 18.750\ cm^3$ $V'' = 18.000\ cm^3$
10,000	0.0909	0.0905	0.0929	0.0920
9,000	.0831	.0832	.0850	.0844
8,000	.0747	.0747	.0764	.0758
7,000	.0652	.0654	.0668	.0663
6,000	.0551	.0552	.0565	.0562
5,000	.0438	.0438	.0451	.0447
4,000	.0313	.0313	.0318	.0322
3,000	.0171	.0166	.0168	.0168
2,000	.0000	.0000	.0000	.0000
1,000	−.0223	−.0211	−.0203	−.0203

TABLE 6. *Compression of natural rubber-sulfur vulcanizates at 81.5° C*

$-\Delta V/V_0$

Pressure	10% S $V_0 = 19.711\ cm^3$ $V'' = 18.489\ cm^3$	13% S $V_0 = 20.003\ cm^3$ $V'' = 18.823\ cm^3$	16% S $V_0 = 18.777\ cm^3$ $V'' = 17.707\ cm^3$	18% S $V_0 = 19.184\ cm^3$ $V'' = 18.129\ cm^3$
atm				
10,000	0.1071	0.1036	0.0975	0.0931
9,000	.0989	.0956	.0901	.0857
8,000	.0911	.0875	.0823	.0779
7,000	.0802	.0781	.0729	.0688
6,000	.0695	.0683	.0636	.0592
5,000	.0559	.0559	.0527	.0484
4,000	.0409	.0408	.0397	.0354
3,000	.0223	.0228	.0227	.0199
2,000	.0000	.0000	.0000	.0000
1,000	−.0286	−.0283	−.0270	−.0281
	20% S $V_0 = 18.765\ cm^3$ $V'' = 17.902\ cm^3$	22% S $V_0 = 19.061\ cm^3$ $V'' = 18.222\ cm^3$	25% S $V_0 = 18.520\ cm^3$ $V'' = 17.724\ cm^3$	28% S $V_0 = 18.942\ cm^3$ $V'' = 18.184\ cm^3$
10,000	0.0914	0.0893	0.0905	0.0913
9,000	.0843	.0818	.0832	.0838
8,000	.0759	.0736	.0748	.0753
7,000	.0663	.0642	.0649	.0657
6,000	.0578	.0542	.0553	.0558
5,000	.0461	.0433	.0440	.0442
4,000	.0335	.0305	.0318	.0302
3,000	.0180	.0166	.0174	.0172
2,000	.0000	.0000	.0000	.0000
1,000	−.0263	−.0244	−.0214	−.0208

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initial volume, V_0, and the fiducial volume at 2,000 atm, V', are given at the head of each column of compressions. Values of V_0 were measured at 21.0° C as described, and the densities so obtained also appear at the head of the columns of data at 21.0° C. Initial volumes at all other temperatures were calculated, using expansivities obtained from the specific volume-temperature curves for rubbers at 1 atm given by Scott. [3].

The reference volume, V', is involved in the calculation of compression and its values are estimated by successive approximations from a generally linear extrapolation of the corresponding calculated compression data. The values of V' finally used agree with corresponding values calculated by extrapolation of empirical equations given by Scott [3] to within a few digits in the second significant figure. Attempts to measure the initial compression, $(V_0-V')/V_0$ were made, using steel piezometers of the type described by Bridgman [6], and the results corroborated the estimated compression to two significant figures. Higher accuracy was not obtainable with the present experimental setup, in which the rigid requirement of monotonic pressure increase could not be met. The values of initial compression finally used were estimated to only two significant figures but are given in table 7 to three significant figures to correspond to the other data. It is to be noted that small variations even in the second significant figure of the initial compression will have no significant effect on the compressions reported in tables 1 to 6, inclusive [4, 5].

TABLE 7. *Initial compression of rubber-sulfur vulcanizates, 1 to 2,000 atm*

$(V_0-V')/V_0$

Temperature	10% S	13% S	16% S	18% S
°C				
10.0	0.0500	0.0400	0.0390	0.0370
21.0	.0510	.0420	.0390	.0370
38.5	.0560	.0540	.0470	.0420
50.2	.0590	.0550	.0510	.0460
64.0	.0590	.0570	.0540	.0490
81.5	.0620	.0590	.0570	.0550
	20% S	22% S	25% S	28% S
10.0				
21.0	0.0370	0.0360	0.0360	0.0350
38.5	.0420	.0400	.0400	.0400
50.2	.0420	.0410	.0410	.0400
64.0	.0440	.0420	.0410	.0400
81.5	.0460	.0440	.0430	.0420

The values of compression shown in tables 1 to 6 are of the same general order of magnitude as those reported by Adams and Gibson [1] and Bridgman [2]. Two sets of duplicate measurements were made at 21.0° C and one at 10° C. These duplicates indicate that the results are reproducible to within a few digits in the fourth decimal place, as has been shown previously [4]. Because the reduction of temperature to 10° C was performed primarily for another purpose, only the rubbers thought to be of particular interest were measured at this temperature. The apparent minimum in compression with increasing sulfur content noted in tables 1 to 6 arises largely from the fact that these data are reckoned from 2,000 atm. If the initial compressions shown in table 7 are added to the corresponding values of tables 1 to 6, the compression reckoned from 1 atm is found to decrease with increasing sulfur contents and appears to approach a relatively constant value at high sulfur contents. The effect of sulfur appears to be largely localized in the low-pressure ranges. With increased temperature, compressions also increase, as expected [7].

5. Empirical Equations

5.1. Isotherms

In the following treatments of the experimental data, the compression is reckoned from 1 atm rather than from 2,000 atm. Values of compression are obtained by adding corresponding data of table 7 and tables 1 to 6. Such a procedure introduces into the data the inherent uncertainty contained in the values of table 7 but in no way affects the validity of any equations applied over elevated pressure ranges and in fact can show little over-all error when applied over the complete pressure range studied here.

Ordinary power series of the type

$$-\Delta V/V_0=A+BP+CP^2+DP^3+ \ . \ . \ . \qquad (1)$$

will not adequately represent the experimental data if only a few terms are included in the equation. For harder rubbers such an equation of third degree in P adequately reproduces the data, but for softer rubbers large deviations occur. The addition of terms as high as the fifth power in P does not radically improve the fit for softer rubbers. Accordingly, the equation proposed by Adams and Gibson [1]

$$-\Delta V/V_0=A+BP+C(1-e^{-DP}) \qquad (2)$$

was used to describe the rubber isotherms of tables 2 to 5. In this equation the exponential term serves to reproduce the large compressions at low pressures but contributes little at the higher pressures.

The method of fitting such an equation to the data differs from that used by Adams and Gibson [1] and is outlined briefly as follows:

The first difference of eq 2 may be written as

$$\Delta=B+CDe^{-DP}, \qquad (3)$$

which reduces at high pressures to

$$\Delta\approx B. \qquad (4)$$

The value of B may, therefore, be estimated by constructing a table of first differences. Using this value of B and taking logarithms of eq (3),

$$\ln(\Delta-B)=\ln CD-DP. \qquad (5)$$

A plot of $\ln(\Delta-B)$ as ordinate versus P as abscissa produces a line whose slope is $-D$. This value of D may be substituted into eq (2), and the resulting equations may be fitted to the data by the method of least squares. The coefficients of eq (2) obtained in this manner are tabulated in table 8 for pressure in units of thousands of atmospheres. These coefficients reproduce the experimental data to within

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TABLE 8 - multiply all A, B, and C values by 10^{-1}

TABLE 8. *Coefficients of isothermal equation* [1]

$-\Delta V/V_0 = A + BP + C(1 - e^{-DP})$

Temperature	10% S				13% S			
	A	B	C	D	A	B	C	D
°C								
21.0	−0.134	0.0742	0.792	0.500	−0.156	0.0713	0.723	0.464
38.5	−.132	.0705	.946	.447	−.0994	.0706	.842	.447
50.2	−.135	.0738	.987	.433	−.128	.0687	.939	.433
64.0	−.134	.0818	.965	.441	−.120	.0726	.956	.435
	16% S				18% S			
	A	B	C	D	A	B	C	D
21.0	−0.0966	0.0747	0.625	0.385	−0.0419	0.0616	0.718	0.258
38.5	−.0377	.0681	.739	.333	−.0740	.0780	.620	.390
50.2	−.0702	.0660	.821	.380	−.0589	.0700	.718	.360
64.0	−.110	.0753	.829	.457	−.0550	.0780	.690	.405
	20% S				22% S			
	A	B	C	D	A	B	C	D
21.0	−0.0401	0.0652	0.686	0.263	−0.0553	0.0653	0.690	0.268
38.5	−.0416	.0745	.641	.333	−.0636	.0720	.673	.324
50.2	−.0583	.0730	.674	.335	−.0444	.0729	.666	.310
64.0	−.0572	.0749	.682	.350	−.0590	.0731	.685	.330
	25% S				28% S			
	A	B	C	D	A	B	C	D
21.0	−0.0880	0.0656	0.721	0.294	−0.0816	0.0731	0.624	0.323
38.5	−.0644	.0735	.671	.324	−.0687	.0716	.691	.324
50.2	−.0543	.0724	.691	.310	−.0847	.0745	.682	.340
64.0	−.0622	.0753	.682	.320	−.0706	.0716	.712	.320

[1] Coefficients are given for pressure in atm×10³.

a few digits in the fourth decimal place and may be used with confidence between 1 and 10,000 atm. It must be emphasized that the equations cannot be expected to reproduce the exact course of the isotherms between 1 and 1,000 atm because no experimental data were obtained at pressures below 1,000 atm.

5.2. Isobars

The arbitrary nature of the determination of D in eq (2) and the compensation of coefficients that occurs in the least-squares fitting precludes use of the coefficients of table 8 in deriving a general equation of state. To obtain constants that might serve such purposes a different method was used.

From the initial weights, volumes, and compressions given, the specific volumes were calculated at each pressure and temperature measured. To each isobar, so obtained, an equation of the type

$$V_{sp} = \alpha + \beta t + \gamma t^2, \tag{6}$$

where t is the temperature in degrees C, was fitted by the method of least squares. A compilation of the coefficients α, β, and γ so obtained is given in table 9.

The coefficients of table 9 reproduce the specific volumes to within ± 0.002 cm³/g and may be used with confidence in the experimental range. Extrapolation, particularly to higher temperatures, is undesirable because of the nature of the equations and the shape of the isobars. For purely isothermal or isobaric purposes the coefficients of tables 8 and 9 are to be preferred to the following equations of state.

TABLE 9. *Coefficients of isobars* [1]

$V_{sp} = \alpha + \beta t + \gamma t^2$

Pressure	10% S 10° C<t<81.5° C			13% S 10° C<t<81.5° C		
	α	β	γ	α	β	γ
atm						
10,000	0.8652	−0.7605×10⁻⁴	1.178×10⁻⁶	0.8563	−3.775×10⁻⁴	4.022×10⁻⁶
9,000	.8728	−.4684	0.739	.8635	−3.577	3.777
8,000	.8807	−.8042	1.378	.8671	−2.044	2.524
7,000	.8881	−.5987	1.772	.8779	−3.195	3.799
6,000	.8959	−.2012	1.751	.8874	−3.718	4.535
5,000	.9062	−.1381	2.304	.8971	−3.323	4.418
4,000	.9158	+1.276	1.514	.9082	−3.409	5.302
3,000	.9265	+3.391	0.190	.9199	−2.704	5.379
2,000	.9415	+5.206	−.606	.9335	−9.530	4.602
1,000	.9662	+6.699	−1.777	.9525	+1.750	2.786
1	.9904	+7.389	−1.135	.9652	+5.502	0.910
	16% S 10° C<t<81.5° C			18% S 21° C<t<81.5° C		
	α	β	γ	α	β	γ
10,000	0.8230	1.742×10⁻⁴	−1.218×10⁻⁶	0.8185	−1.395×10⁻⁴	2.696×10⁻⁶
9,000	.8328	1.827	−1.310	.8297	−2.749	3.794
8,000	.8392	2.291	−1.644	.8325	−0.797	1.894
7,000	.8447	3.699	−2.883	.8322	+3.010	−1.424
6,000	.8540	3.406	−2.443	.8407	−0.900	2.411
5,000	.8635	3.815	−2.924	.8510	−1.055	2.421
4,000	.8761	3.298	−2.146	.8719	−0.992	2.494
3,000	.8883	3.096	−1.238	.8865	−2.009	3.945
2,000	.9030	3.110	−0.104	.9018	−2.275	4.820
1,000	.9175	6.119	−2.035	.9141	+1.530	3.923
1	.9354	6.721	−0.954	.9298	+4.716	5.204

See footnote at end of table.

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TABLE 9. *Coefficients of isobars* [1]—Continued

$V_{sp}=\alpha+\beta t+\gamma t^2$

	20% S, 10° C<t<81.5° C			22% S, 21° C<t<81.5° C		
	α	β	γ	α	β	γ
10,000	0.8071	-2.077×10^{-4}	4.076×10^{-6}	0.8082	-7.061×10^{-4}	8.899×10^{-6}
9,000	.8137	−1.754	3.736	.8130	−6.310	8.303
8,000	.8201	−1.226	3.332	.8212	−6.572	8.615
7,000	.8269	−0.802	3.146	.8323	−7.845	9.856
6,000	.8344	−.056	2.312	.8390	−7.059	9.227
5,000	.8442	+.117	2.320	.8469	−5.809	8.008
4,000	.8563	+.239	2.270	.8587	−6.255	8.580
3,000	.8683	+.260	2.380	.8699	−5.308	7.712
2,000	.8824	+.089	3.158	.8841	−5.249	7.874
1,000	.9048	−4.457	9.790	.9004	−5.020	8.452
1	.9142	+1.851	2.687	.9128	−2.983	6.932
	25% S, 21° C<t<81.5° C			28% S, 21° C<t<81.5° C		
	α	β	γ	α	β	γ
10,000	0.7896	-2.048×10^{-4}	3.114×10^{-6}	0.7890	-2.407×10^{-4}	3.318×10^{-6}
9,000	.7946	−4.770	5.450	.7760	−2.407	3.318
8,000	.7981	−3.171	3.968	.7831	−2.527	3.629
7,000	.8051	−3.234	4.225	.7953	−4.393	5.384
6,000	.8143	−2.952	4.004	.7990	−1.925	3.041
5,000	.8232	−2.252	3.325	.8068	−1.174	2.445
4,000	.8334	−1.851	2.992	.8189	−2.118	3.689
3,000	.8458	−1.567	2.659	.8268	+5.117	0.861
2,000	.8614	−1.851	2.992	.8434	−0.451	2.073
1,000	.8813	−2.996	4.399	.8589	−.146	2.049
1	.8901	+0.217	2.030	.8709	+1.698	0.798

[1] Temperature in degrees C in the specified range.

5.3. Equations of State

To obtain a PVT equation of state the coefficients β and γ given in table 9 for a particular rubber were each fitted to an equation of the type

$$\beta \text{ or } \gamma = a+bP+cP^2+dP^3. \tag{7}$$

The values of a, b, c, and d so obtained were used to recalculate values of β and γ at each pressure. The calculated β and γ values were used with the observed V_{sp} values to calculate corrected values of α, which were then fitted by least squares to a cubic in pressure. The correction applied to values of α was in most instances negligible. However, the values of α are not designed to correspond to the values of table 9 but rather to produce correct values of V_{sp}. As α, β, and γ have been defined as coefficients of t in eq 6, the 12 values of a, b, c, and d may be utilized to formulate an empirical equation of state. These equations and their known limits of accuracy follow:

For 10 percent of sulfur:

$$V_{sp}=0.9904-3.107\times10^{-5}P+3.688\times10^{-9}P^2-1.857\times10^{-13}P^3+(7.389\times10^{-6}-9.098\times10^{-9}P-1.926\times10^{-12}P^2+2.110\times10^{-16}P^3)t+(-1.135\times10^{-6}+7.591\times10^{-10}P-2.045\times10^{-14}P^2+3.764\times10^{-18}P^3)t^2. \tag{8}$$

$1<P<10{,}000$ atm; $10° \text{ C}<t<81.5° \text{ C}$; deviation from observed values increases at highest temperature and lowest pressure. Except at highest temperature and lowest pressure, deviation is ±0.45 percent.

For 13 percent of sulfur:

$$V_{sp}=0.9652-1.648\times10^{-5}P+5.786\times10^{-10}P^2-1.551\times10^{-15}P^3+(5.502\times10^{-6}-4.654\times10^{-7}P+7.677\times10^{-11}P^2-3.958\times10^{-15}P^3)t+(0.9103\times10^{-6}+2.899\times10^{-9}P-5.939\times10^{-13}P^2+3.355\times10^{-17}P^3)t^2. \tag{9}$$

$1<P<10{,}000$ atm; $10° \text{ C}<t<81.5° \text{ C}$; maximum deviation from observed values ±0.33 percent.

For 16 percent of sulfur:

$$V_{sp}=0.9354-1.694\times10^{-5}P+4.338\times10^{-10}P^2+1.840\times10^{-14}P^3+(6.72\times10^{-6}-1.953\times10^{-7}P+3.617\times10^{-11}P^2-2.207\times10^{-15}P^3)t+(-0.954\times10^{-6}-4.336\times10^{-10}P+4.623\times10^{-14}P^2-5.74\times10^{-19}P^3)t^2. \tag{10}$$

$1<P<10{,}000$ atm; $10°\ C<t<81.5°\ C$; maximum deviation from observed values ± 0.37 percent.

For 18 percent of sulfur:

$$V_{sp}=0.9298-1.633\times10^{-5}P+3.15\times10^{-10}P^2+2.29\times10^{-14}P^3+(4.716\times10^{-4}-4.604\times10^{-7}P+9.934\times10^{-11}P^2-6.078\times10^{-15}P^3)t+(5.204\times10^{-6}-9.780\times10^{-11}P-2.082\times10^{-13}P^2+2.011\times10^{-17}P^3)t^2. \quad (11)$$

$1<P<10{,}000$ atm; $21°\ C<t<81.5°\ C$; equation deviates sharply at highest temperature at lowest pressure. Except at highest temperature and lowest pressure, deviation from observed values is ± 0.75 percent.

For 20 percent of sulfur:

$$V_{sp}=0.9142-2.084\times10^{-5}P+1.554\times10^{-9}P^2-4.78\times10^{-14}P^3+(1.851\times10^{-4}-7.855\times10^{-8}P+1.859\times10^{-11}P^2-1.559\times10^{-15}P^3)t+(2.687\times10^{-6}+1.182\times10^{-9}P-4.099\times10^{-13}P^2+2.967\times10^{-17}P^3)t^2. \quad (12)$$

$1<P<10{,}000$ atm; $10°\ C<t<81.5°\ C$; maximum deviation from observed values, ± 0.87 percent.

For 22 percent of sulfur:

$$V_{sp}=0.9128-1.483\times10^{-5}P+2.90\times10^{-10}P^2+1.45\times10^{-14}P^3+(-2.98\times10^{-4}-1.336\times10^{-7}P+1.543\times10^{-11}P^2-5.85\times10^{-16}P^3)t+(6.932\times10^{-6}+3.574\times10^{-10}P+1.575\times10^{-14}P^2-3.506\times10^{-18}P^3)t^2. \quad (13)$$

$1<P<10{,}000$ atm; $21°\ C<t<81.5°\ C$; maximum deviation from observed values, ± 0.37 percent.

For 25 percent of sulfur:

$$V_{sp}=0.8901-1.562\times10^{-5}P+5.11\times10^{-10}P^2+1.1\times10^{-15}P^3+(0.217\times10^{-4}-1.054\times10^{-7}P+1.064\times10^{-11}P^2-3.436\times10^{-16}P^3)t+(2.030\times10^{-6}+4.047\times10^{-10}P-2.59\times10^{-15}P^2-1.86\times10^{-18}P^3)t^2. \quad (14)$$

$1<P<10{,}000$ atm; $21°\ C<t<81.5°\ C$; maximum deviation from observed values ± 0.25 percent. Most figures show deviations of ± 0.12 percent or less.

For 28 percent of sulfur:

$$V_{sp}=0.8709-1.486\times10^{-5}P+5.61\times10^{-10}P^2-8.8\times10^{-15}P^3+(1.698\times10^{-4}-1.264\times10^{-7}P+1.017\times10^{-11}P^2-1.659\times10^{-16}P^3)t+(0.798\times10^{-6}+7.786\times10^{-10}P-4.074\times10^{-14}P^2-1.217\times10^{-18}P^3)t^2. \quad (15)$$

$1<P<10{,}000$ atm; $21°\ C<t<81.5°\ C$; maximum deviation from observed values, ± 0.37 percent.

The derivation of eq (8) to (15) represents the main objective of the present report. The equations have not been examined critically in a mathematical sense. Physically, the signs and courses of the first partial derivatives are in agreement with expectations, and no singularities are observed in the experimental range. It is believed that these equations may be used with confidence for subsequent calculation purposes where either the isobaric or isothermal equations cannot be used.

It appears that the process of generalization may be carried one step further whereby each of the 12 coefficients in eq (8) to (15) can be related to a linear or quadratic expression of sulfur content. This would reduce the 8 equations containing 96 coefficients to a single general equation of at most 36 coefficients. Such a reduction may be useful for some purposes but can be deferred until such time as data are available on rubbers of lower sulfur content.

A valid comparison of the present data and those of Scott is not feasible as the experimental pressure ranges do not overlap. Generalizing on the basis of a limited number of tests that have been made, the following observations may be made: Extrapolation of Scott's equations to 1,000 atm produces data that are in generally good agreement with the data observed here. Such an extrapolation, it is to be noted, represents a rather considerable extension of the pressure interval employed by Scott.

For information concerning the behavior of rubber at low pressures, the data of Scott are considered preferable to those reported here, which may not be expected to closely reproduce the PVT behavior below 1,000 atm. For pressures above 1,000 atm, the equations given by Scott cannot be considered reliable, and the present equations are to be preferred.

The author is indebted to W. H. Leser for valuable suggestions concerning the fitting of empirical equations to the data.

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6. References

[1] L. H. Adams and R. E. Gibson, J. Wash. Acad. Sci. **20,** 213 (1930).
[2] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76,** 9 (1945).
[3] A. H. Scott, J. Research NBS **14,** 100 (1935) RP760.
[4] C. E. Weir, J. Research NBS **46,** 207 (1951) RP2192.
[5] C. E. Weir, J. Research NBS **45,** 468 (1950) RP2160.
[6] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **47,** 347 (1911).
[7] P. W. Bridgman, The physics of high pressure (G. Bell & Sons, Ltd., London, 1949).

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On a Recursion Formula and on Some Tauberian Theorems[1]

N. G. de Bruijn[2] and P. Erdös[3]

The paper is concerned with two sets of positive numbers, c_k and f_k, connected by a linear recursion formula. Under certain assumptions there exists an asymptotic relation between the partial sums $\sum_1^n c_k$ and $\sum_1^n f_k$.

The assumptions on the c_k are of Tauberian type. The method is based on discussing the associated power series $\sum_1^\infty c_k x^k$ and $\sum_1^\infty f_k x^k$.

Let

$$c_k \geq 0, \quad \sum_{k=1}^{\infty} c_k = 1.$$

Define

$$f(1)=1, \quad f(n)=\sum_{k=1}^{n-1} c_k f(n-k) \qquad (n>1). \tag{1}$$

This recursion formula has various applications in the theory of probability.[4] In the present note, however, we will investigate (1) independently of its applications. Assume, first, that

$$\sum_{k=1}^{\infty} k c_k < \infty.$$

Erdös, Feller, and Pollard [2] proved that if the greatest common divisor of the k's with $c_k>0$ is 1, then,

$$f(n) \to A^{-1} \qquad (A=\sum_{k=1}^{\infty} k c_k). \tag{2}$$

It is easy to see that if the greatest common divisor of the k's with $c_k>0$ is greater than 1, then $\lim f(n)$ cannot exist.[5] It was also shown that if

$$\sum_{1}^{\infty} k c_k = \infty,$$

then (2) always holds, in other words, $f(n)\to 0$.

Feller in a paper [3] restricted himself to the case when $\sum k c_k < \infty$. In the present paper we will not in general make this assumption.

We prove the following results:

Theorem 1. *Assume that for every* $k>1$,

$$c_{k-1} c_{k+1} > c_k^2. \tag{3}$$

Then for every $n>1$,

$$f(n-1) f(n+1) > f^2(n).$$

Other theorems of the same type as theorem 1 were proved by T. Kaluza [4]. Assuming (1), he showed for instance, that $f(2)>0$, $f(n-1)f(n+1)>f^2(n)$ $(n=2,3,\ldots)$ imply that the c's are positive. Furthermore, he proved that $f(1), f(2), \ldots$ is a moment sequence if, and only if, $c_1, c_2, c_3, \ldots$ is a moment sequence. (Here $c_1, c_2, c_3, \ldots$ is called a moment sequence whenever it is of the form $\alpha_n = \int_0^\infty u^n d\chi(u)$, where $\chi(u)$ is nondecreasing and such that the integral converges for all n).

Theorem 2. *Put* $r_k = \sum_{l \geq k} c_l$, $s(y) = \sum_{k \leq y} r_k$, $S(y) = \sum_{k \leq y} f(k)$. *Assume that for every* $p>0$

$$\lim_{y \to \infty} \frac{s(py)}{s(y)} = p^\alpha \tag{4}$$

for a fixed α, $0 \leq \alpha \leq 1$ (α *independent of* p). Then

$$s(y) S(y) = \frac{y}{\Gamma(2-\alpha)\Gamma(1+\alpha)} + o(y). \tag{5}$$

Theorem 3. *Assume that* (3) *and* (4) *both hold. Then,*

$$f(n) = \frac{1-\alpha}{s_n \Gamma(1+\alpha)\Gamma(2-\alpha)} + o\left(\frac{1}{s_n}\right). \tag{6}$$

In case $\alpha=1$, (6) does not give an asymptotic formula, it only gives $f(n)=o(s_n^{-1})$.

It would be interesting to obtain conditions that imply $f(n+1)/f(n)\to 1$. We can prove that if $c_{n+1}/c_n \to 1$, then $f(n+1)/f(n)\to 1$; also if

$$c_n < B. \min_{1 \leq k \leq n} c_k,$$

then $f(n+1)/f(n)\to 1$. We suppress the proofs because we believe that very much more general conditions can be obtained. If $f(n+1)/f(n)\to 1$, then it is not difficult to prove that $c_{n-1}=o\{f(n)\}$. It can be conjectured that the converse is also true, under the additional condition that the g.c.d of the k's with $c_k>0$ is 1.

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[4] See Feller [3]. This paper quotes most of the literature that deals with these questions.

[5] See [2] and the remarks at the end of the present paper.

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Proof of theorem 1. First we show that for any n

$$c_n\{f(n+2)f(n)-f^2(n+1)\}$$

$$=\sum_{k=2}^{n}(c_{n+1}c_{k-1}-c_nc_k)\{f(n+1)f(n+1-k)$$

$$-f(n)f(n+2-k)\}. \quad (7)$$

To prove (7) split the right-hand side into four sums. These are, respectively,

$$c_{n+1}f(n+1)\sum_{k=2}^{n}c_{k-1}f(n+1-k)=c_{n+1}f(n+1)f(n);$$

$$-c_{n+1}f(n)\sum_{k=2}^{n}c_{k-1}f(n+2-k)$$

$$=-c_{n+1}f(n)\{f(n+1)-c_nf(1)\};$$

$$-c_nf(n+1)\sum_{k=2}^{n}c_kf(n+1-k)$$

$$=-c_nf(n+1)\{f(n+1)-c_1f(n)\};$$

$$c_nf(n)\sum_{k=2}^{n}c_kf(n+2-k)$$

$$=c_nf(n)\{f(n+2)-c_{n+1}f(1)-c_1f(n+1)\}.$$

Addition gives $c_n\{f(n+2)f(n)-f^2(n+1)\}$, which proves (7).

To prove theorem 1, observe that

$$f(1)f(3)-f^2(2)=c_1f(2)+c_2f(1)-f^2(2)=c_2f(1)>0.$$

((3) implies that all the c's are positive.) Assume now $n>2$, and suppose that $f(k)f(k+2)>f^2(k+1)$ is already proved for $1\leq k<n$. Then (3) implies $c_{n+1}c_{k-1}>c_nc_k$, since by (3) $(c_2/c_1)<(c_3/c_2)<\ldots$. Thus in (7) all terms on the right side are positive, and we obtain $f(n)f(n+2)>f^2(n+1)$, which proves theorem 1.

Remarks: It is clear from the proof of theorem 1 that if we only assume that $c_{k+1}c_{k-1}\geq c_k^2$ $(k>1)$, we obtain $f(n+1)f(n-1)\geq f^2(n)(n>1)$.

If (3) is true, then, by theorem 1, $f(n+1)/f(n)$ is an increasing function of n. We have $f(n+1)/f(n)<1$ for all n, for otherwise we would have $f(n+1)/f(n)>a>1$ for some a and all large n. This would contradict the fact that $f(n)=O(1)$, which easily follows from (1). From $f(n+1)<f(n)$ $(n=1,2,\ldots)$ it follows that

$$f(n)(c_1+\ldots+c_n)<f(n+1)<f(n), \quad (8)$$

and so (3) implies $f(n+1)/f(n)\to 1$ $(n\to\infty)$.

To prove theorem 2 we need some lemmas.

Lemma 1.[6] *Let $d_1, d_2, \ldots$ be an infinite sequence, and let α be a number greater than -1. Put $g(y)=\sum_{k\leq y}d_k$, and assume that $g(y)>0$ for all large y, and that, for every $p>0$,*

$$g(py)/g(y)\to p^\alpha \qquad (y\to\infty). \quad (9)$$

Then the series $D(x)=\sum_1^\infty d_kx^k$ converges for $|x|<1$, and if $t>0$, $t\to 0$, we have

$$D(e^{-t})=\{1+o(1)\}g(1/t)\Gamma(1+\alpha). \quad (10)$$

Proof. The function $L(y)=g(y)y^{-\alpha}$ is positive for y large, and it is measurable and bounded over any finite interval $0\leq y\leq A$ (for $g(y)=0$ if $0\leq y<1$). Furthermore, $L(y)$ is slowly increasing, that is, $L(py)/L(y)\to 1$ as $y\to\infty$, for every $p>0$.

We shall prove that for any $\epsilon>0$ there exist positive constants $C(\epsilon)$, $C_1(\epsilon)$ such that

$$\left|\frac{L(py)}{L(y)}\right|<C_1(\epsilon)\{p^\epsilon+p^{-\epsilon}\} \quad (p>0,\ y>C(\epsilon)). \quad (11)$$

It is known[7] that $L(py)/L(y)\to 1$ as $y\to\infty$, uniformly for $a\leq p\leq b$, where a and b are arbitrary positive. Therefore, $C(\epsilon)$ can be determined such that $L(y)>0$ for $y\geq C(\epsilon)$ and such that

$$\log\{L(py)/L(y)\}<\epsilon \qquad (e^{-1}\leq p\leq e, y\geq C(\epsilon)).$$

It follows by induction that

$$\log\{L(py)/L(y)\}<\epsilon(1+\log p) \quad (p\geq 1, y\geq C(\epsilon)), \quad (12)$$

and

$$\log\{L(py)/L(y)\}<\epsilon(1+\log p^{-1})$$

$$(C(\epsilon)y^{-1}\leq p\leq 1, \quad y\geq C(\epsilon)). \quad (13)$$

Put

$$M(\epsilon)=\sup_{0\leq y\leq C(\epsilon)}L(y).$$

Then we have, for $0<p<C(\epsilon)y^{-1}$, $y\geq C(\epsilon)$ by (13),

$$\left.\begin{aligned}&\log\{L(py)/L(y)\}\\&=\log\{L(C(\epsilon))/L(y)\}+\log\{L(py)/L(C(\epsilon))\}\\&<\epsilon\left\{1+\log\frac{y}{C(\epsilon)}\right\}+\log\frac{M(\epsilon)}{L(C(\epsilon))}\\&<\epsilon(1+\log p^{-1})+C_2(\epsilon).\end{aligned}\right\} \quad (14)$$

Now (12), (13) and (14) prove (11).

In the first place, we obtain from (11) that $L(x)=O(x^\epsilon)$ as $x\to\infty$, and therefore $d_k=O(k^{\alpha+\epsilon})$. Hence the power series for $D(x)$ converges if $|x|<1$.

We have, for $t>0$,

$$D(e^{-t})=\int_0^\infty e^{-yt}dg(y)=\int_0^\infty te^{-yt}g(y)dy,$$

[6] As far as the authors know, a complete proof of this lemma was not published before, although it is the Abelian counterpart of the Tauberian lemma 2, which is due to Karamata. K. L. Chung brought to our notice that in Doetsch [1] an incomplete proof is presented for a theorem very similar to our lemma 1. Doetsch claims to use only the inequalities $L(y)=O(y^\epsilon)$, $1/L(y)=O(y^\epsilon)$ $(y\to\infty)$, whereas an inequality of the type (11) seems to be indispensable.

[7] See [5] (where $L(y)$ is assumed to be continuous), and [7].

and so,

$$D(e^{-t})=t^{-\alpha}L(t^{-1})\int_0^\infty \phi(y,t)dy,$$

where

$$\phi(y,t)=e^{-y}y^\alpha\frac{L(y/t)}{L(1/t)}.$$

For any fixed $y>0$, $\phi(y,t)$ tends to $e^{-y}y^\alpha$ as $t\to 0$. Furthermore, by (11), $\phi(y,t)$ can be majorized by a positive function of y only, whose integral over $(0,\infty)$ converges. Therefore, by the Arzéla-Lebesgue theorem, we have

$$\int_0^\infty \phi(y,t)dy\to\int_0^\infty e^{-y}y^\alpha dy=\Gamma(1+\alpha)\quad(t>0,t\to 0).$$

This proves the lemma.

Lemma 2. *Assume that*

$$D(x)=\sum_1^\infty d_k x^k$$

is convergent for $|x|<1$, *and that* $d_k\geq 0$ *but not all* $d_k=0$. *Let* $\alpha\geq 0$ *be fixed. Assume that for any fixed* $p>0$

$$D(e^{-pt})/D(e^{-t})\to p^{-\alpha}\quad(t>0,t\to 0).\tag{15}$$

Then we have

$$\sum_{k\leq t^{-1}}d_k=\{1+o(1)\}D(e^{-t})/\Gamma(1+\alpha)\quad(t>0,t\to 0).$$

This result is due to Karamata [6].

Theorem 2 can be derived from lemmas 1 and 2. Following a suggestion of Karamata, we first prove a more general theorem:

Theorem 4. *Let* $a_k\geq 0$ (*but not all*$=0$), $b_k\geq 0$ (*but not all*$=0$), $k=1,2,3,\ \ldots$;

$$d_n=\sum_1^{n-1}a_k b_{n-k}\quad(n=2,3,\ \ldots).$$

Put

$$s(y)=\sum_{k\leq y}a_k,\quad S(y)=\sum_{k\leq y}b_k,\quad T(y)=\sum_{k\leq y}d_k.$$

Assume that for every $p>0$, *we have*

$$s(py)/s(y)\to p^\alpha,\quad T(py)/T(y)\to p^\gamma\quad(y\to\infty),$$

where $\gamma\geq\alpha\geq 0$, γ *and* α *independent of* p. *Then we have*

$$S(y)=\left\{1+o(1)\right\}\frac{T(y)}{s(y)}\cdot\frac{\Gamma(1+\gamma)}{\Gamma(1+\gamma-\alpha)\Gamma(1+\alpha)}.$$

Proof. Put $A(x)=\sum_1^\infty a_k x^k$, $B(x)=\sum_1^\infty b_k x^k$, $D(x)=\sum_1^\infty d_k x^k$, then we have formally $A(x)B(x)=D(x)$. Both $A(x)$ and $D(x)$ are analytic for $|x|<1$ (see lemma 1); it follows that $B(x)$ is analytic in some circle $|x|<\delta$. The coefficients of $B(x)$ are non-negative, and for $0\leq x<1$, $B(x)$ is analytic (since $A(x)>0$ for $0<x<1$). Thus by a theorem of Pringsheim (see [8], sec. 17) $B(x)$ is analytic for $|x|<1$.

By lemma 1 we have, as $t>0$, $t\to 0$,

$$A(e^{-t})\sim s(t^{-1})\Gamma(1+\alpha);\quad D(e^{-t})\sim T(t^{-1})\Gamma(1+\gamma).$$

Hence for any $p>0$,

$$B(e^{-pt})/B(e^{-t})\to p^{\gamma-\alpha}.$$

But then by lemma 2

$$S(t^{-1})\sim B(e^{-t})/\Gamma(1+\gamma-\alpha).$$

Now theorem 4 follows immediately from $D(x)=A(x)B(x)$.

Proof of theorem 2. Theorem 2 is an easy consequence of theorem 4. If

$$F(x)=f(1)x+f(2)x^2+\ \ldots,\quad R(x)=r_1x+r_2x^2+\ \ldots,$$

then it follows from (1) that $F(x)R(x)=x^2/(1-x)$, and so

$$\sum_{k=1}^{n-1}r_k f(n-k)=1\quad(n=2,3,\ \ldots).\tag{16}$$

Therefore, taking

$$a_k=r_k,\quad b_k=f(k)\quad(k=1,2,\ \ldots),$$
$$d_n=1\quad(n=2,3,\ \ldots),\quad\gamma=1,$$

we obtain from theorem 4

$$S(n)\sim\frac{n}{s(n)}\cdot\frac{\Gamma(2)}{\Gamma(2-\alpha)\Gamma(1+\alpha)},$$

which proves theorem 2.

Proof of theorem 3. Let ϵ be a number greater than 0. From (8) we infer

$$f(n)>\{S_{n(1+\epsilon)}-S_n\}/(\epsilon n+1).\tag{17}$$

It follows from (4) and (5) that

$$s_n S_n\sim Cn,\quad s_n S_{n(1+\epsilon)}\sim Cn(1+\epsilon)^{1-\alpha},$$

where $C=1/\{\Gamma(2-\alpha)\Gamma(1+\alpha)\}$. Therefore, (17) implies

$$\liminf f(n)s_n\geq C\{(1+\epsilon)^{1-\alpha}-1\}/\epsilon\quad(n\to\infty).$$

This holds for every $\epsilon>0$. Making $\epsilon\to 0$, we obtain

$$\liminf f(n)s_n\geq(1-\alpha)C.$$

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Applying the same argument to $n(1-\epsilon)$ instead of $n(1+\epsilon)$ we obtain $\liminf f(n)s_n \leq (1-\alpha)C$. This proves theorem 3.

Some final remarks: Feller [3] proved the following theorem: Assume that the g.c.d. of the k's with $c_k>0$ is 1, and that

$$\sum_1^\infty k^2 c_k < \infty, \tag{18}$$

then

$$\sum_{l=1}^{n} f(l) = A^{-1}n + d + o(1), \tag{19}$$

where $A=\sum_1^\infty kc_k$, and, in fact, $\sum_1^\infty \{f(l)-A^{-1}\}<\infty$. Now we show the converse, namely, if (19) holds, then (18) holds too.

Theorem 5. Assume that the g.c.d. of the k's with $c_k>0$ is 1, and that $\sum_1^\infty k^2 c_k = \infty$. Then we have

$$\sum_1^\infty \{f(l)-A^{-1}\} = \infty.$$

Proof. If $A=\infty$, then (19) expresses that $\sum_1^\infty f(l)<\infty$. This is false, since $\sum_1^\infty f(l)x^l = x/\{1-\sum_1^\infty c_k x^k\}$, and the right-hand side tends to ∞ if $x\to 1$.

Now assume $A<\infty$. Since $f(l)\to A^{-1}$, we have by (16),

$$\begin{aligned}\sum_1^n f(l)\cdot\sum_1^n r_k &= \sum_{2\leq k+l\leq n} f(l)r_k + \sum_{l=1}^{n} f(l)\sum_{n+1-l}^{n} r_k \\ &= n-1+\sum_{l=1}^{n}(A^{-1}+\epsilon_l)\sum_{n+1-l}^{n} r_k \\ &= n-1+A^{-1}\sum_{k=1}^{n} kr_k + \sum_{l=1}^{n}\epsilon_l \sum_{n+1-l}^{n} r_k \\ &= n-1+\Sigma_1+\Sigma_2.\end{aligned}$$

We have $\Sigma_1\to\infty$, since $\sum kr_k$ diverges ($\sum kr_k > \frac{1}{2}\sum k^2 c_k$), and $\Sigma_2 = o(\Sigma_1)$, since $\epsilon_l\to 0$. Finally, we have $\sum_1^\infty r_k = \sum_1^\infty kc_k = A$, and so

$$A\sum_1^n f(l) > n + \Sigma_1 + o(\Sigma_1).$$

Consequently,

$$\sum_1^n \{f(l)-A^{-1}\} > \{A^{-1}+o(1)\}\Sigma_1 \to \infty,$$

q.e.d.

Let D denote the greatest common factor of the k's with $c_k>0$. Erdös, Feller, and Pollard [2] proved that if $D=1$ and $\sum kc_k<\infty$, then

$$\sum_2^\infty |f(k)-f(k-1)| < \infty, \tag{20}$$

which, of course, implies that $f(k)$ tends to a limit. It seems possible that the condition $\sum kc_k<\infty$ is superfluous.

If $D>1$ and $\sum kc_k<\infty$, then (20) does not hold, since $\lim f(k)$ does not exist. In order to see this, take $c_k^* = c_{kD}$, $f^*(k)=f(kD-D+1)$; it follows that

$$f^*(k)\to(\textstyle\sum kc_k^*)^{-1} = DA^{-1}.$$

Hence,

$$f(kD+1)\to DA^{-1}\neq 0, \quad f(kD+2)\equiv 0.$$

If $D>1$ and $\sum kc_k=\infty$, then we have $f(k)\to 0$. Nevertheless, the series (20) need not converge. Take $c_n=0$ for n odd, $c_n = 24\pi^{-2}n^{-2}$ for n even. Then we have $f(2n)=0$, $f(2n-1)=f^*(n)$, where $f^*(n)$ and $c_n^* = c_{2n}$ are related by an equation of the type (1), and $\sum_1^\infty c_n^* = 1$. It follows, by theorem 3, that $f^*(n)\sim \pi^2/(6\log n)$.

Therefore,

$$f(2n-1)\sim \pi^2/(6\log n), f(2n)=0,$$

and the series (20) diverges.

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[1] Doetsch, Theorie und Anwendung der Laplace-Transformationen (Springer, Leipzig, 1937).

[2] P. Erdös, W. Feller and H. Pollard, A property of power series with positive coefficients, Bul. Am. Math. Soc. **55**, 201–204 (1949). See also, Kolmogorov Bul. de l'Université d'État à Moscow, Sec. A. **1**, 1–15 (1937).

[3] W. Feller, Fluctuation theory of recurrent events, Trans. Am. Math. Soc. **67**, 98–119 (1949).

[4] T. Kaluza, Ueber die Koeffizienten reziproker Funktionen, Math. Z. **28**, 161–170 (1928).

[5] J. Karamata, Sur un mode de croissance régulière des fonctions, Mathematica (Cluj) **4**, 38–53 (1930).

[6] J. Karamata, Neuer Beweis und Verallgemeinerung der Tauberschen Sätze, welche die Laplacesche und Stieltjessche Transformation betreffen, J. Reine Angew. Math. **164**, 27–39 (1931).

[7] J. Korevaar, T. van Aardenne-Ehrenfest and N. G. de Bruijn, A note on slowly oscillating functions, Nieuw. Arch. Wiskunde (2) **23**, 77–86 (1949).

[8] E. Landau, Darstellung und Begründung einiger neuerer Ergebnisse der Funktionentheorie, (Springer, Berlin, 2e Aufl. 1929).

Los Angeles, August 10, 1950.

Pyrolysis of Styrene, Acrylate, and Isoprene Polymers in a Vacuum*[1]

S. Straus and S. L. Madorsky

Pyrolysis was carried out in a vacuum in the temperature range 250° to 400° C. The volatile products were collected and fractionated. The more volatile products were analyzed in the mass spectrometer, whereas the less volatile products were tested for their average molecular weights.

In the styrene group of polymers, poly-alpha-methylstyrene yielded practically 100 percent of monomer, and poly-meta-methylstyrene and poly-alpha-deuterostyrene yielded about 52 and 70 percent, respectively, of monomer or similar products, the other volatiles consisting of dimer, trimer, and some tetramer. Hydrogenated polystyrene yielded volatiles consisting of 6 percent of small molecules and a mixture of products of average molecular weight of 602.

In the acrylate group of polymers, benzoyl peroxide polymerized polymethyl methacrylate, molecular weight 150,000, and thermally prepared polymethyl methacrylate, molecular weight 5,100,000, yielded almost 100 percent of monomer. Polymethyl acrylate yielded carbon dioxide, methanol, and a mixture of various fragments, of average molecular weight of 686.

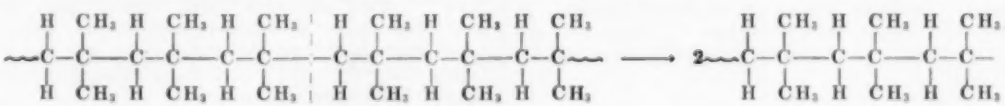
In the isoprene group of polymers, synthetic polyisoprene, natural rubber (*cis*-polyisoprene), and gutta hydrocarbon (*trans*-polyisoprene), yielded isoprene, dipentene, and mixtures of large molecules of average molecular weight of about 600.

1. Introduction

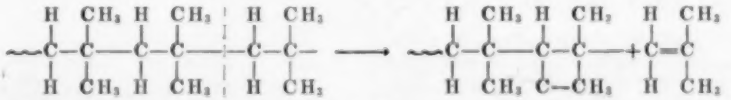
In two previous papers [1, 2][2] a new method for the pyrolysis of polymers has been described. These polymers included polystyrene, polyisobutene, polyisoprene, polybutadiene, GR–S and polyethylene. It was found that in the temperature range of about 300° to 450° C these polymers break up into volatile fragments varying in size from a monomer to products of molecular weight of about 1,000. It was also found that in all cases, except polybutadiene, composition and relative amounts of the volatile products, in the temperature range covered, were independent of temperature or extent of volatilization. In case of polybutadiene, while the nature of the volatile compounds was the same their relative amounts varied.

There appears to be a fundamental difference in the behavior of the various polymers during pyrolysis This difference is in the ratio between the amount of monomer or similar fragments, on the one hand, and that of larger fragments in the volatile products, on the other. For example, in the case of polyethylene, the amount of smaller molecules is equal to about 3 weight percent, or 21 mole percent, of the total volatilized part. For polyisobutene this amount is 32 weight percent, or 78 mole percent. Free radicals, once formed, can either split off monomer units or abstract a hydrogen from other chains or possibly its own chain. The less favorable the conditions are in the polymer for the abstraction process (transfer) the higher is the probability of producing monomer. When a break occurs in a polyethylene chain there is a sufficient supply of susceptible hydrogen [3, 4] on the same chain or on the other chains in the neighborhood of the break to saturate the free radical ends.

In the case of polyisobutene, saturation of the free radical ends cannot take place as readily as in polyethylene, first, because hydrogen atoms on the chains are less abundant, and second, because of steric hindrance of the methyl groups on the chains. As a result, free radical ends, formed by rupture of bonds during pyrolysis, serve as starting points for monomer formation:



and



* This work was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[1] This paper was presented at the 122d meeting of the American Chemical Society in Atlantic City, N. J., Sept. 14 to 19, 1952.

[2] Figures in brackets indicate the literature references at the end of this paper.

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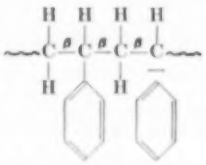
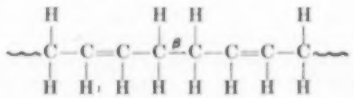
This process will continue in the manner of a zip reaction until the chain is consumed, or until the free radical becomes saturated.

Another fundamental difference between polyethylene and polyisobutene lies in their relative C—C bond strength. In polyethylene all the bonds, except those at the ends, are normal paraffin bonds, whereas in polyisobutene the bonds are weaker because they are adjacent to tertiary carbons. The same is true of polystyrene, where every bond in the chain is adjacent to a secondary carbon. An additional weakness in the polystyrene chain molecule is caused by the double bonds of the benzene ring. These double bonds tend to weaken the C—C bond in the beta position, thus



This is also true of polybutadiene



and polyisoprene.

In the present work a study was made of the effect of variations in the side groups of a polymer on thermal stability and nature and relative amounts of the volatile fragments. Three types of polymers were selected for this purpose:

1. The polystyrene type, including poly-meta-methylstyrene, poly-alpha-deuterostyrene, poly-alpha-methylstyrene, and hydrogenated polystyrene.

2. The acrylate type, including benzoyl peroxide polymerized polymethyl methacrylate A, molecular weight 150,000, thermally prepared polymethyl methacrylate B, molecular weight 5,100,000, and polymethyl acrylate.

3. The isoprene type, including synthetic polyisoprene, natural rubber (*cis*-polyisoprene), and gutta hydrocarbon (*trans*-polyisoprene).

Pyrolysis of polyisoprene has been described in a previous paper [2]. The investigation has now been extended to include the isoprene-dipentene ratio in the volatile products. Pyrolysis of some of the above polymers has been investigated recently by others [5, 6, 7].

2. Apparatus and Experimental Procedure

The molecular still used for the pyrolysis of polymers in this investigation was the same as was used in the previous work [1, 2]. It consists of a Dewar-like Pyrex-glass apparatus made of two concentric parts jointed by ground waxed flanges. All the polymers were used in the form of a 2-percent solution in benzene. The solution was spread in a platinum tray, and most of the solvent was evaporated in a vacuum of about 10 to 15 mm Hg at room temperature. The tray was then preheated in a vacuum of about 10^{-3} to 10^{-4} mm Hg at 100° to 130° C to a constant weight. This usually required about 2 hr. The dry sample weight was from 20 to 60 mg. It was found that when the sample was larger, for the size of the tray used in this work, spattering resulted during pyrolysis.

The tray was placed on top of an electric heater in the pyrolysis apparatus evacuated to about 10^{-6} mm Hg. The sample was heated up to the maximum temperature of a given experiment during a period of 45 min, and this temperature was then maintained for 30 min. Precautions were taken against desorption of gases from the wall of the apparatus in the neighborhood of the electric heater, by first flaming gently the outside of the Dewar-like apparatus and then raising a water thermostat against the apparatus so that the level of the water reached above the level of the enclosed heater. Temperature of pyrolysis was read by means of a Pt-PtRh thermocouple spot-welded to the tray at its center.

The method employed in this investigation is designated as pyrolytic fractionation [1]. The volatile products are fractionated for two reasons: (1) to be able to differentiate between monomer or monomer-size molecules, on the one hand, and the larger fragments in the volatiles, on the other, and (2) to facilitate mass-spectrometric analysis of the more volatile products. The following fractions were collected:

I. *Hard glass-like residue in the tray.*—This fraction was weighed and its solubility in ordinary organic solvents determined. Nothing further was done with this fraction. It is planned to study in the near future the average molecular weight of the residues as a function of temperature and extent of degradation. For this purpose larger samples will be pyrolyzed in a larger apparatus.

II. *Wax-like fraction, volatile at the temperature of pyrolysis, but not at room temperature.*—This fraction was weighed and analyzed for average molecular weight by Rast's microcryoscopic method in cyclohexane, benzene, or camphor. Rast's method [8] was checked by the present authors on a number of pure compounds. The results of this check, with C_6H_{12} and C_6H_6 as solvents, were reported previously [2]. In checking this method the values used for F, the molecular freezing-point lowering, were 20.0° and 5.12° C for C_6H_{12} and C_6H_6, respectively. In the case of camphor as solvent, a check was made with pure nonacosane, molecular weight 409, as solute. Using the value of 39.7° C for F, the results of two sets of determinations were

1	2
420	409
386	409
415	400
Average..... 407	406

The molecular weight of fraction II from polymethyl acrylate was determined by a method involving rates of isothermal distillation in a vacuum, developed by G. Gee [9] and modified by D. J. Crawley and S. G. Weissberg [10], using toluene as solvent.

III. *Liquid fraction volatile at room temperature, but not at the temperature of liquid nitrogen.*—This fraction was weighed and was then analyzed in the mass spectrometer. It consisted, in the case of some polymers, of the monomer only; in the case of other polymers, also of dimer, trimer, and fragments of monomer, dimer and trimer. To facilitate further the mass-spectrometer analysis, fraction III in some cases was again fractionated into a lighter fraction IIIA, containing mostly the monomer-size fragments, and a heavier fraction IIIB, containing mostly the dimer-size fragments. Separation into IIIA and IIIB was carried out at −80° C by a method described in a previous publication [2]. Composition of IIIA and IIIB was determined by mass-spectrometer analysis. In some cases where fraction III or IIIA was large, or where it was suspected to contain compounds larger than the monomer, the sample was expanded into a larger volume by a method described previously [1]. This step was found useful, because the presence of heavier molecules is masked in mass-spectrometer analysis by the lighter molecules when the total pressure is too high.

IV. *Gaseous fraction, volatile at the temperature of liquid nitrogen.*—This fraction in all cases was of the order of about 0.1 percent of the total volatilized part and consisted of traces of CH_4, CO_2, and CO, as determined by mass-spectrometer analysis. The weight of this fraction was calculated from its volume, pressure, and composition.

3. Pyrolysis of Styrene Polymers

3.1. Poly-meta-methylstyrene

A pure grade of poly-meta-methylstyrene, containing some para-methylstyrene as part of its structure, was used. It was prepared by the Dow Chemical Co. by low-temperature polymerization and had an average molecular weight of 450,000, as determined by the light-scattering method.[3] Results of seven experiments ranging from 309° to 399° C are shown in table 1. The amount of fraction III in weight percent of the volatilized part remained almost constant throughout the temperature range. Fraction III was analyzed, without further fractionation, in the mass spectrometer. Results of four analyses are shown in table 2. In experiment 7, fraction III was expanded into a 700-ml volume before it was analyzed. All four analyses gave similar results.

Fraction II was tested for average molecular weight by the microcryoscopic method in C_6H_{12} solution. The average of three determinations was

TABLE 1. *Pyrolitic fractionation of styrene polymers*

Experiment	Weight of sample	Temperature	Fractions in weight percent of original sample			Fraction III in weight percent of total volatalized part
			I Residue	II Nonvolatile at room temperature	III Volatile at room temperature	
Poly-meta-methylstyrene						
	mg	*° C*	*wt %*	*wt %*	*wt %*	*wt %*
1	18.3	309	98.3	(*)	(*)	(*)
2	25.0	329	87.6	6.0	6.4	51.6
3	22.7	356	56.1	21.8	22.1	50.4
4	24.4	369	24.6	37.4	38.0	50.3
5	23.2	387	3.7	45.7	50.6	52.5
6	28.4	391	1.4	46.5	52.1	52.9
7	25.5	399	0.4	46.4	53.2	53.4
Average						51.8±1.1
Poly-alpha-deuterostyrene						
1	16.7	334	95.8	3.1	1.1	(*)
2	39.1	351	75.0	7.4	17.6	70.3
3	17.4	355	71.8	8.9	19.3	68.4
4	24.2	365	42.2	18.9	38.9	67.3
5	16.0	367	40.9	15.3	43.8	74.1
6	21.2	377	13.0	26.6	60.4	69.4
7	20.1	380	8.2	28.3	63.5	69.2
8	21.4	387	1.7	27.1	71.2	72.5
Average						70.2±1.8
Poly-alpha-methylstyrene						
1	23.1	259	97.4	.....	2.4	91.7
2	30.6	279	68.7	.....	29.5	94.3
3	27.3	299	20.6	.....	74.3	93.6
4	33.7	329	0.4	.....	85.1	85.4
5	34.7	329	.2	.....	96.3	96.4
6	14.1	329	.3	.....	97.6	97.9
7	18.6	329	.3	.....	99.0	99.2
8	24.2	344	0.	.....	93.8	93.8
9	15.9	349	0.	.....	93.9	93.9
Average						94.0±2.6
Hydrogenated polystyrene						
1	18.1	335	87.1	12.1	0.8	6.6
2	20.1	349	76.6	21.7	1.7	5.5
3	18.9	369	47.9	48.7	3.4	6.5
4	16.9	379	23.6	72.7	3.7	5.2
5	19.2	384	12.5	81.9	5.6	6.4
6	24.6	391	6.3	88.9	4.8	5.2
Average						5.9±0.6

* Too small to be accurately determined.

[3] Work on molecular-weight determinations by the light-scattering method was carried out by M. Wales and L. C. Williams of the Polymer Structure Section of the National Bureau of Standards.

TABLE 2. *Mass-spectrometer analysis of fraction III obtained in the pyrolysis of poly-meta-methylstyrene*

Component	Analysis of fraction III in experiments—				Average of experiments 2, 3, 5, 7	Average for total volatilized part
	2	3	5	7		
	Mole%	*Mole%*	*Mole%*	*Mole%*	*Mole%*	*Wt%*
Xylene	16.3	20.4	8.1	16.8	15.5	7.3
Meta-methylstyrene	83.7	79.6	91.9	83.2	84.5	44.5
Total	100.0	100.0	100.0	100.0	100.0	51.8

355, as shown in table 3. The gaseous fractions IV from experiments 2, 3, 5, and 7 were analyzed in the mass spectrometer. There was no CH_4 present, but only traces of CO and CO_2. The CO might have come from oxygen as an impurity in the polymer, and the CO_2 was the background in the mass spectrometer. Fraction I was soluble in cold benzene.

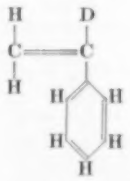
TABLE 3. *Molecular weights of fractions II obtained in the pyrolysis of polymers*

Polymer	Solvent	Average molecular weight
Polyethylene [a]	Camphor	692
Polyisobutene	Cyclohexane	543
Hydrogenated polystyrene	do	602
Polystyrene	do	264
Poly-meta-methylstyrene	do	355
Poly-alpha-deuterostyrene	do	271
Polymethyl acrylate	Toluene [b]	633
Polymethyl methacrylate A	Camphor	686
Polyisoprene	Cyclohexane	577
trans-Polyisoprene	Benzene	554
cis-Polyisoprene	Camphor	616
Polybutadiene	Cyclohexane	739

[a] Values for polyethylene, polyisobutene, polystyrene, polyisoprene, and polybutadiene were taken from previous publications [1, 2].
[b] The isothermal distillation method was used for polymethyl-acrylate.

3.2. Poly-alpha-deuterostyrene

The alpha-deuterostyrene monomer



was prepared [4] by reacting lithium-aluminum deuteride with acetophenone. The polymer was prepared thermally at 70° C. It had a molecular weight of 1,260,000 as determined by light scattering. Pyrolysis was carried out in the temperature range 334° to 387° C. The results are shown in table 1. The average value of fraction III is 70.2±1.8 weight percent of the total volatilized part, as compared with 42 for polystyrene [1] or 51.8 for poly-meta-methylstyrene.

Results of mass-spectrometer analysis of fraction III, from experiments 2, 5, and 7, are shown in table 4. This fraction consisted mainly of the monomer and small amounts of styrene and alpha-methylstyrene. In the case of fraction III from two experiments, the tubes containing them were opened in air and loss of weight was plotted as a function of time, in the same manner as described in a previous paper on pyrolysis of polystyrene [1]. The resulting curves indicated the absence of fragments heavier than the monomer. In view of this, separation of fraction III into IIIA and IIIB was not undertaken.

[4] This polymer, as well as polymethyl methacrylate B and polymethyl acrylatel were prepared by L. A. Wall of the Polymer Structure Section of the National Bureau of Standards.

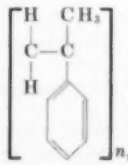
TABLE 4. *Mass-spectrometer analysis of fraction III obtained in the pyrolysis of poly-alpha-deuterostyrene*

Component	Analysis of fraction III in experiments—			Average of experiments 2, 5, 7	Average for total volatilized part
	2	5	7		
	Mole %	*Mole %*	*Mole %*	*Mole %*	*wt%*
Styrene	2.5	1.8	2.3	2.2	1.5
Alpha-deuterostyrene	96.9	96.6	97.4	97.0	68.1
Alpha-methylstyrene	0.6	1.6	0.3	0.8	0.6
Total	100.0	100.0	100.0	100.0	70.2

The wax-like fraction II from experiments 4, 6, and 8 was found to have an average molecular weight of 271, as shown in table 3. The gaseous fraction IV from experiments 3, 4, and 5 was analyzed in the mass spectrometer. Only traces of air, CO, and CO_2 were found. The residue, fraction I, was soluble in cold benzene.

3.3. Poly-alpha-methylstyrene

Poly-alpha-methylstyrene,



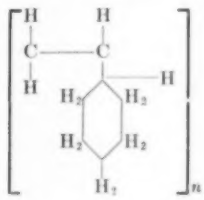
in the form of flakes, was obtained from the Dow Chemical Co. It was prepared by low-temperature polymerization and had a molecular weight of 350,000 as determined by light scattering. Results of nine experiments, in the temperature range 259° to 349° C, are given in table 1. Fraction III represents, on the average, 94.0±2.6 percent of the total volatilized part. Mass-spectrometer analysis of this fraction showed the presence of only the monomer. By evaporating fraction III from small tubes in air, it was found that the dimer was absent. The residue was soluble in cold benzene.

There was no indication of a fraction II on the condenser of the pyrolysis apparatus. Because the gaseous fraction IV is less than 0.1 percent of the volatiles, it can be assumed that poly-alpha-methylstyrene, on pyrolysis, yields almost 100 percent of monomer, although the collection of the monomer was incomplete in the experiments shown in table 1.

Jellinek [6] heated poly-alpha-methylstyrene, of about 70,000 molecular weight, in a vacuum in order to determine the rate of degradation. He used a temperature range of 280° to 363° C and reports that the rate of production of monomer was very fast, but he does not indicate whether fragments other than monomer were formed.

3.4. Hydrogenated Polystyrene

The hydrogenated polystyrene



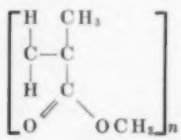
was obtained from the Federal Telecommunications Laboratory in the form of a very fine powder. It had a molecular weight of 82,000, as determined by light scattering. This polymer is very soluble in benzene. Results of six pyrolysis experiments in the temperature range 335° to 391° C are shown in table 1. Fraction III is very small and, on the average, amounts to 5.9 ± 0.6 percent of the total volatilized part. In this respect it resembles polyethylene, where fraction III is 3.4 percent [2]. A quantitative analysis of fraction III could not be obtained in the mass spectrometer because of lack of mass spectra of some of the components. However, mass-spectrometer analysis of fraction III from experiments 4, 5, and 6 indicated the presence of the following compounds in the order of abundance as given: Cyclohexene, cyclohexane, methyl cyclohexene, methyl cyclohexane, vinyl cyclohexene, vinyl cyclohexane, and ethyl cyclohexane.

Fraction II from experiments 4, 5, and 6 was found to have, on the average, a molecular weight of 602, as shown in table 3. Fraction IV was very small, and on mass-spectrometer analysis was found to contain a trace of air and CO_2, but no CH_4 or H_2. The residue was soluble in cold benzene.

4. Pyrolysis of Acrylate Polymers

4.1. Polymethyl Methacrylate A

This polymer was a benzoyl peroxide polymerized polymethyl methacrylate, analyzing 0.6 percent of benzoyl peroxide and having a molecular weight of 150,000, as determined by the light-scattering method.



Results of pyrolysis experiments in the temperature range 140° to 318° C are shown in table 5. On the average, fraction III represented about 96 percent and fraction II about 4 percent of the total volatilized part. Fraction III consisted of monomer only. Fraction II was collected and tested for average molecular weight. The results showed a molecular weight of 686 (see table 3). Fraction IV was less than 0.1 percent of the volatiles. Mass-spectrometer analysis showed it to consist of CO and CO_2. The residue was soluble in benzene.

TABLE 5. *Pyrolytic fractionation of acrylate polymers*

Experiment	Weight of sample	Temperature	Fractions in weight percent of original sample			Fraction III in weight percent of total volatilized part
			I	II	III	
			Residue	Nonvolatile at room temperature	Volatile at room temperature	
Polymethyl methacrylate A (molecular weight 150,000)						
	mg	*° C*	*wt %*	*wt %*	*wt %*	*wt %*
1	[a] 82.8	140	97.7	.....	.....	.....
2	101.9	152	89.5	.....	.....	.....
3	121.2	206	82.5	.....	.....	.....
4	117.4	216	79.5	.....	.....	.....
5	101.9	268	61.7	1.8	36.5	95.3
6	139.6	273	56.1	2.5	41.4	94.3
7	231.5	285	53.5	2.1	44.4	95.5
8	149.8	318	25.7	2.2	72.1	97.1
Average						95.5 ±0.4
Polymethyl methacrylate B (molecular weight 5,100,000)						
1	42.5	246	96.4	.....	3.0	83.0
2	44.6	259	95.6	.....	3.8	86.6
3	46.9	279	93.4	.....	5.4	82.2
4	18.0	279	92.8	.....	6.8	95.4
5	41.5	281	90.1	.....	8.3	83.7
6	57.5	304	78.2	.....	20.4	93.8
7	44.7	304	76.7	.....	21.8	93.1
8	16.0	319	64.8	.....	34.4	95.8
9	19.9	324	59.6	.....	40.1	99.1
10	44.7	330	28.5	.....	66.5	93.1
11	19.1	349	13.4	.....	84.6	97.6
12	42.4	354	2.8	.....	86.9	89.3
Average						91.1 ±5.1
Polymethyl acrylate						
1	24.6	292	90.2	6.9	2.9	30.0
2	27.7	300	81.5	12.7	5.8	31.6
3	50.5	309	79.5	13.2	7.3	35.6
4	21.9	324	61.0	28.4	10.6	27.0
5	23.9	325	65.2	26.2	8.6	24.7
6	25.6	329	25.9	53.0	21.1	28.4
7	42.9	334	23.4	53.9	22.7	29.7
8	21.7	354	15.7	62.9	21.4	25.4
9	22.0	359	15.7	65.2	19.1	22.6
10	20.7	361	10.8	67.7	21.5	24.1
11	40.6	369	10.1	68.2	21.7	24.3
12	19.0	374	6.9	71.4	21.7	23.3
13	42.9	379	7.7	71.1	21.2	22.9
14	23.3	399	3.2	73.9	22.9	23.9
Average						26.7 ±3.2

[a] In this series of experiments a larger pyrolysis apparatus and a larger tray were used than used in the other experiments.

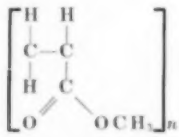
4.2. Polymethyl Methacrylate B

This polymer was prepared by polymerizing the monomer, without the use of a catalyst, at 25° C, precipitating, and then washing the precipitate several times with methanol. The methanol was removed by evacuation at 60° C for 48 hr. The molecular weight, as determined by light scattering, was 5,100,000. Results of experiments in the temperature range 246° to 354° C are shown in table 5.

Fraction III is on the average 91.1 ±5.1 percent of the total volatilized part. Analysis of this fraction from experiments 1, 2, 3, 6, and 10 showed it to consist entirely of the monomer. Here, as in the case of poly-alpha-methylstyrene, there was no wax-like deposit on the condenser of the pyrolysis apparatus to indicate the presence of a wax-like fraction II. Therefore, the same assumption can be made here that this polymer yields on pyrolysis about 100 percent of monomer, although the collection, as shown in table 5, was not complete.

4.3. Polymethyl Acrylate

The polymethyl acrylate



was prepared by polymerizing the monomer in benzene solution at 70° C, using 0.1 mole percent of benzoyl peroxide as catalyst. The polymer was precipitated, then washed several times, with methanol, and dried to a constant weight. Results of 14 pyrolysis experiments, in the temperature range 292° to 399° C, are shown in table 5. Fraction III, on the average amounts to 26.7 ±3.2 percent of the volatilized part. It was found by preliminary analysis of this fraction in the mass spectrometer that it contained a considerable amount of CO_2, which interfered with the analysis of the other constituents. Fraction III was, therefore, separated into fraction IIIA, which contained most of the CO_2, and IIIB, which contained the less volatile constituents. This separation was carried out at −80° C. On the average, IIIA amounted to 5.5 percent and IIIB to 21.2 percent of the total volatized part. Mass-spectrometer analyses are shown in table 6. Fraction IIIA contained mostly CO_2, but also small amounts of ethanol, ethane, and ethylene, while IIIB contained mostly ethanol, mixed with small amounts of CO_2, methyl acrylate, methyl methacrylate, and some oxygenated C_4 to C_8 compounds. It is rather surprising that, instead of the monomer, as in polymethyl methacrylate, fraction III consisted mainly of CO_2 and CH_3OH.

The wax-like fraction II was tested for molecular weight by the isothermal distillation method. The average of four tests, as shown in table 3, was 633. The residue was soluble in cold benzene. The gaseous fraction IV consisted of small amounts of CO, CO_2, and CH_4.

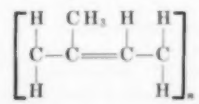
TABLE 6. *Mass-spectrometer analysis of fractions IIIA and IIIB obtained in the pyrolysis of polymethyl acrylate*

Component	Analysis of fraction IIIA in experiments—				Average of experiments 1, 7, 10, 13	Average for total volatilized part
	1	7	10	13		
	Mole %	*Mole %*	*Mole %*	*Mole %*	*Mole %*	*Wt %*
Ethylene	.....	0.7	.....	1.5	0.6	Trace
Ethane	.....	.....	.....	0.5	Trace	Do.
CH_3OH	3.7	.....	0.5	.....	1.1	0.1
CO_2	96.3	99.3	99.5	98.0	98.3	5.4
Total	100.0	100.0	100.0	100.0	100.0	5.5
	Analysis of fraction IIIB in experiments—				Average of experiments 1, 3, 5, 10, 13	
	1	3	5	10	13	
CH_3OH	88.3	77.9	84.5	85.4	77.7	82.6	14.5
CO_2	.....	16.7	5.1	6.9	12.4	8.3	2.0
Methyl acrylate	1.2	.....	3.9	2.5	....	1.5	0.7
Methylmethacrylate	0.5	.....	0.4	0.3	.....	0.2	0.1
Oxygenated compounds C_4 to C_8	10.0	5.4	6.1	5.1	9.9	7.4	3.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	21.2

5. Pyrolysis of Isoprene Polymers

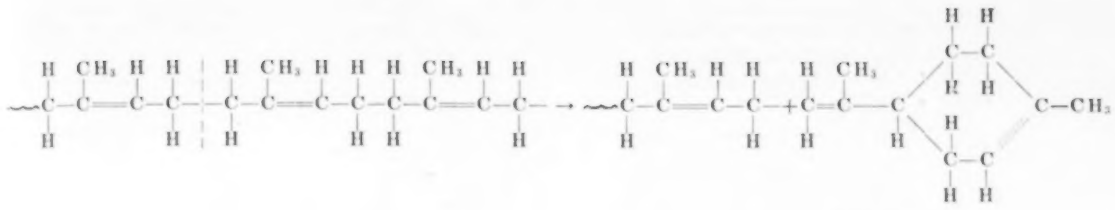
5.1. Synthetic Polyisoprene

Pyrolysis of polyisoprene



was carried out previously by the present authors [2], but the monomer-dimer ratio in fraction III was not thoroughly investigated at that time. This ratio has now been studied in more detail. The same material was used as in the previous work. Results of 11 pyrolysis experiments are shown in table 7. The relative amount of fraction III in the volatiles is greater in the early stages of degradation, the same as was found previously, and the average amount in experiments where volatilization was about 68 percent or more is 12.2±0.6 percent of the total pyrolyzed part, as compared with 11.3±0.4 percent found previously.

It has been known for a long time that isoprene and dipentene are some of the volatile products of thermal degradation of rubber. Dipentene is a dimer of isoprene and could form when a dimer splits off the end of a chain:



dipentene

Fraction III was separated into IIIA and IIIB at −80° C. It was found necessary to extend the time of collecting the lighter fraction IIIA, at the temperature of liquid nitrogen, from a few minutes, as was done in other cases, to 30 min, in order to get a complete separation. Both fractions were analyzed in the mass spectrometer. The results of analysis of fraction IIIA are shown in table 8. Fraction IIIB consisted mainly of dipentene, mixed with small amounts of its isomers and with paramenthene, $C_{10}H_{18}$. Table 9 shows the relative amounts of monomer and dipentene in percentage of total volatilized part. As seen from this table, the amount of isoprene remains almost constant, whereas the amount of dipentene decreases with increasing temperature of degradation.

TABLE 7. *Pyrolytic fractionation of isoprene polymers*

Experiment	Weight of sample	Temperature	Fractions in weight percent of original sample: I Residue	II Nonvolatile at room temperature	III Volatile at room temperature	Fraction III in weight percent of total volatilized part
Synthetic polyisoprene						
	mg	*° C*	*wt %*	*wt %*	*wt %*	*wt %*
1	59.1	309	78.7	17.4	3.9	18.1
2	50.2	314	73.2	22.4	4.4	16.8
3	55.5	317	68.6	25.9	5.5	17.6
4	46.6	320	55.7	37.6	6.7	16.1
5	54.5	333	31.8	59.4	8.8	13.0
6	28.1	336	25.0	65.8	9.2	12.2
7	50.6	340	23.4	66.3	10.3	12.9
8	48.8	351	13.4	77.1	9.5	11.0
9	32.5	367	6.4	81.7	11.9	12.7
10	42.8	399	4.3	84.6	11.1	11.9
11	47.0	399	4.9	84.1	11.0	11.6
Average						[a] 12.2 ±0.6
Natural rubber (*cis*-polyisoprene)						
1	40.8	287	95.0	2.5	2.5	[b]
2	47.8	302	85.5	10.3	4.2	29.3
3	30.4	309	79.2	15.7	5.1	24.5
4	59.9	311	72.1	21.5	6.4	23.6
5	44.7	313	68.1	24.5	7.4	23.1
6	47.4	314	70.7	23.3	6.0	20.5
7	44.9	314	65.9	27.0	7.1	22.1
8	49.0	318	57.1	33.3	9.6	23.1
9	51.2	319	68.0	24.1	8.9	27.7
10	33.5	321	52.3	36.5	11.2	23.6
11	50.3	326	43.5	44.8	11.7	21.5
12	42.9	326	21.8	63.8	14.4	18.5
13	28.7	329	26.3	60.3	13.4	18.2
14	23.5	329	28.3	60.0	11.7	16.4
15	43.2	350	18.8	67.5	13.7	17.5
16	39.9	331	25.7	60.4	13.9	18.8
17	27.6	349	5.8	77.3	16.9	17.9
18	44.2	352	4.8	78.1	17.1	18.0
19	43.8	352	4.7	79.3	16.0	16.9
20	41.4	367	1.6	80.5	17.9	18.2
Average						21.0 ±3.1

TABLE 7. *Pyrolytic fractionation of isoprene polymers*—Con.

Experiment	Weight of sample	Temperature ° C	Fractions in weight percent of original sample: I Residue	II Nonvolatile at room temperature	III Volatile at room temperature	Fraction III in weight percent of total volatilized part
Gutta hydrocarbon (*trans*-polyisoprene)						
1	47.3	309	90.6	8.1	1.3	[b]
2	26.9	316	64.7	26.9	8.4	19.6
3	38.8	317	63.5	29.3	7.2	20.7
4	34.0	317	61.8	30.1	8.1	21.1
5	48.6	322	65.0	29.1	5.9	22.7
6	20.3	329	25.1	62.9	12.0	16.0
7	26.1	329	21.5	66.0	12.5	16.0
8	23.5	354	5.3	78.0	16.7	17.2
9	38.8	355	8.6	75.6	15.8	17.3
10	50.1	357	3.4	79.2	17.4	18.0
11	24.5	364	3.0	79.7	17.3	17.6
Average						18.6 ±1.9

[a] This average is for experiments 5 to 11, inclusive, where the residue was less than 32 percent.
[b] Too small to be accurately determined.

TABLE 8. *Mass-spectrometer analysis of fraction IIIA obtained in the pyrolysis of synthetic polyisoprene*

Component	Analysis of fraction IIIA in experiments— 3	6	9	Average of experiments 3, 6, 9	Average for total volatilized part
	Mole %	*Mole %*	*Mole %*	*Mole %*	*wt %*
Isoprene	90.6	94.2	92.7	92.5	3.2
Pentenes	3.8	2.2	5.4	3.8	0.1
Dipentene and its isomers	Trace	Trace	Trace	Trace	Trace
Other hydrocarbons [a]	5.6	3.6	1.9	3.7	0.1
Total	100.0	100.0	100.0	100.0	3.4

[a] Includes butenes, butane, hexadiene, and cyclohexadiene.

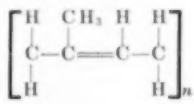
TABLE 9. *Distribution of monomer and dimer in fraction III obtained in the pyrolysis of synthetic polyisoprene*

Experiment	Temperature	Total volatilized in weight percent of sample	Total fraction III	Monomer	Dimer
			In weight percent of volatilized part		
	°C	wt %	wt %	wt %	wt %
1	309	21.3	18.1	3.4	14.7
2	314	26.8	16.8	3.1	13.7
4	320	44.3	16.1	3.3	12.8
7	340	76.6	12.9	3.2	9.7
10	369	95.7	12.0	3.7	8.3
11	369	95.1	11.6	3.5	8.1

The average molecular weight of fraction II from polyisoprene has been reported in a previous publication [2]. It was determined in a solution of cyclohexane and was found to be 577. Mass-spectrometer analysis of fraction IV has also been reported previously. This fraction was found to consist of methane.

5.2. Natural Rubber (*cis*-Polyisoprene)

Pale crepe rubber [5]



was extracted for 96 hr in a Soxhlet apparatus in an atmosphere of CO_2 and washed with benzene. This treatment removes most of the resinous material but not the protein. The solvents were evaporated at 60° to 70° C. The results of 20 pyrolysis experiments are shown in table 7. Here, as in isoprene, the relative amount of fraction III is higher in the early stages of degradation. On the average, fraction III amounts to 21.0 ±3.1 percent of the total volatilized part.

Fraction III was separated at −80° C by 30-min fractionation into IIIA and IIIB. Results of mass-spectrometer analysis of fraction IIIA are shown in table 10. Fraction IIIB was also analyzed in the mass spectrometer and was found to contain mostly dipentene, mixed with a small amount of its isomers and with *p*-menthene. Table 11 shows relative amounts of isoprene and dipentene in percentage of total volatilized part. Here again the amount of isoprene is independent of temperature of pyrolysis, while the amount of dipentene decreases with increase of temperature. However, on the whole, the dipentene content is higher in the case of *cis*-polyisoprene than it is in the case of synthetic polyisoprene.

TABLE 10. *Mass-spectrometer analysis of fraction IIIA obtained in the pyrolysis of natural rubber (cis-polyisoprene)*

Component	Analysis of fraction IIIA in experiments—				Average of experiments 3, 6, 13, 14	Average for total volatilized part
	3	6	13	14		
	Mole %	Mole %	Mole %	Mole %	Mole %	Wt. %
Isoprene	97.1	98.3	97.1	96.0	97.1	3.8
Pentenes	1.9	1.7	2.6	3.4	2.4	0.1
Dipentene and its isomers	0.3	Trace	Trace	....	0.1	Trace
Other hydrocarbons *	.7	....	0.3	0.6	.4	Do.
Total	100.0	100.0	100.0	100.0	100.0	3.9

* Includes butenes, butane, hexadiene, and cyclohexadiene.

TABLE 11.—*Distribution of monomer and dimer in fraction II obtained in the pyrolysis of natural rubber (cis-polyisoprene)*

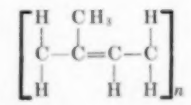
Experiment	Temperature	Total volatilized in weight percent of sample	Total fraction III	Monomer	Dimer
			In weight percent of volatilized part		
	° C	Wt %	Wt %	Wt %	Wt %
4	311	27.9	23.6	4.1	19.5
7	314	34.1	22.1	3.9	18.2
8	318	42.9	23.1	4.1	19.0
11	326	56.5	21.5	3.8	17.7
15	330	81.2	17.5	3.8	13.7
19	352	95.3	16.9	3.9	13.0

Fraction III was separated into IIIA and IIIB during 30 min at −80° C. Mass-spectrometer analysis of IIIA is shown in table 12, and relative amounts of isoprene and dipentene are shown in table 13. In respect to isoprene-dipentene ratios, *trans*-polyisoprene resembles more closely *cis*-polyisoprene than synthetic polyisoprene. Fraction IIIB contained mainly dipentene, mixed with small amounts of its isomers and para-menthene.

Fraction II was soluble in benzene, and its molecular weight was determined in this solvent. The average of four determinations was 554, as shown in table 3. Fraction IV here again was very small and contained CO, CO_2, and air. The residue was soluble in cold benzene.

5.3. Gutta Hydrocarbon (*trans*-polyisoprene)

Gutta hydrocarbon



or *trans*-polyisoprene was purified in the same manner as *cis*-polyisoprene. Results of 11 pyrolysis experiments are shown in table 7. Fraction III comprised, on the average, 18.6±1.9 percent of the total pyrolyzed part. Fraction III was separated into IIIA and IIIB during 30 min at −80° C. Mass-spectrometer analysis of IIIA is shown in table 12, and relative amounts of isoprene and dipentene are shown in table 13. In respect to isoprene-dipentene ratios, *trans*-polyisoprene resembles more closely *cis*-polyisoprene than synthetic polyisoprene. Fraction IIIB contained mainly dipentene, mixed with small amounts of its isomers and para-menthene.

Fraction II was soluble in benzene, and its molecular weight was determined in this solvent. The average of four determinations was 554, as shown in table 3. Fraction IV here again was very small and contained CO, CO_2, and air. The residue was soluble in cold benzene.

[5] Purification of *cis*-rubber, as well as of *trans*-rubber, was carried out by M. Tryon of the Rubber Section of the National Bureau of Standards.

TABLE 12. *Mass-spectrometer analysis of fraction IIIA obtained in the pyrolysis of gutta hydrocarbon (trans-polyisoprene)*

Component	Analysis of fraction IIIA in experiments—					Average of experiments 4, 5, 6, 8, 9	Average for total volatilized part
	4	5	6	8	9		
	Mole %	*Mole* %	*Mole* %	*Mole* %	*Mole* %	*Mole* %	Wt. %
Isoprene	91.5	98.0	97.3	96.0	97.1	96.0	2.9
Pentenes •	6.7	Trace	.....	0.9	.....	1.5	Trace
Dipentene and its isomers	1.8	2.0	2.7	3.1	2.9	2.5	0.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	3.0

• Includes also small amounts of other C_5 and of C_6 hydrocarbons.

TABLE 13. *Distribution of monomer and dimer in fraction III obtained in the pyrolysis of gutta hydrocarbon (trans-polyisoprene)*

Experiment	Temperature	Total volatilized in weight percent of sample	Total fraction III	Monomer	Dimer
			In weight percent of volatilized part		
	°C	*wt* %	*wt* %	*wt* %	*wt* %
2	316	35.3	19.6	3.0	16.6
3	317	36.5	20.7	3.0	17.7
7	329	78.5	16.0	2.9	13.1
11	364	97.0	17.6	3.2	14.4

6. Discussion of Results

In the styrene group of polymers, poly-alpha-deuterostyrene and poly-meta-methylstyrene resemble polystyrene [1] in their pattern of thermal degradation. All three polymers yield a considerable amount of monomer and a fraction II, which has an average molecular weight about one-half as large as in the case of other polymers investigated (table 3). This low molecular weight of fraction II can be accounted for only by assuming that it consists of a mixture of dimer, trimer, and some tetramer [11]. Poly-alpha-methylstyrene, on the other hand, resembles polymethyl methacrylate in yielding almost 100 percent of monomer.

A summary of monomer fraction yield for all polymers of this investigation, and for polyethylene, polyisobutene, polystyrene, and polybutadiene, in a previous investigation [1, 2], is given in table 14. In the second column of this table the yield is expressed in weight percent and in the third column, in mole percent of the volatilized part.

In the case of polymethyl methacrylate, the benzoyl peroxide catalyzed polymer A, molecular weight 150,000, yielded on pyrolysis 96 weight percent of monomer and 4 weight percent of nonmonomer-size molecules. The thermally prepared polymer B, molecular weight 5,100,000, yielded almost 100 percent of monomer. However, the more surprising difference in the behavior of these two polymers is the fact that polymer A pyrolyzed at temperatures of about 50° to 60° C lower than polymer B (see table 5, also fig. 1). As was pointed out in another paper [11], this difference is due mainly to the different methods by which the polymers were prepared and not to the differences in their molecular weights.

TABLE 14. *Amount of monomeric fraction obtained in the pyrolysis of polymers*

Polymer	Monomeric fraction in percentage of volatilized part	
	Wt %	*Mole* %
Polyethylene	3	21
Hydrogenated polystyrene	6	25
Polyisobutene	32	78
Polystyrene	42	65
Poly-meta-methylstyrene	52	77
Poly-alpha-deuterostyrene	70	86
Poly-alpha-methylstyrene	100	100
Polymethyl acrylate •	27	.....
Polymethyl methacrylate A	96	99
Polymethyl methacrylate B	100	100
Polybutadiene	14	57
Synthetic polyisoprene	12	42
trans-Polyisoprene	19	55
cis-Polyisoprene	21	59

• In view of the fact that fraction III from this polymer contained a large amount of CO_2 and MeOH, the mole percent of the monomeric fraction could not be calculated.

In hydrogenated polystyrene the conditions approach those of polyethylene. The yield of monomeric molecules is small, and its amount is constant in percentage of total volatilized part (table 1); also, fraction II has a high molecular weight.

Polymethyl acrylate resembles the other vinyl polymers in one respect, that the amount of fraction III (table 5) is independent of temperature or extent of volatilization. In respect to composition of this fraction, however, this polymer differs radically from the other polymers. Fraction III from methyl acrylate pyrolysis consists mainly of CO_2 and CH_3OH, which are fragments of the carboxylic side groups. The monomer appears to the extent of only a few percent.

In the isoprene group of polymers, the pattern of breakup is almost the same for the three polymers. The differences appear in the amount of fraction III, this being 12, 19, and 21 weight percent, or 42, 55, and 59 mole percent, of total volatilized part in synthetic polyisoprene, *trans*-polyisoprene, and *cis*-polyisoprene, respectively. The yield of isoprene is about the same in all three polymers, so that the differences in fraction III are due to differences in the yield of dipentene. On the basis of tables 9, 11, and 13, the average weight ratios of dipentene to isoprene are: for synthetic polyisoprene, from 4.3:1 at 309° C to 2.3:1 at 369° C; for *cis*-polyisoprene, from 4.8:1 at 311° C to 3.3:1 at 352° C; for *trans*-polyisoprene, from 5.5:1 at 316° C to 4.5:1 at 364° C. On the whole, there is a close resemblance in the behavior of the three isoprene polymers during thermal degradation. However, there is a closer resemblance between the two natural rubbers in regard to the amount of dipentene formed.

A comparison of thermal stability of 10 polymers studied in this paper and of 4 polymers and 1 copolymer studied previously [1, 2] is shown in figures 1

and 2. The curves are based on experiments carried out under similar conditions. The curves for polyisoprene polymers are shown separately in figure 2 because they would appear too crowded if included in figure 1.[6]

Fraction III or IIIA obtained in the pyrolysis of polymers gives on mass-spectrometer analysis a characteristic spectrum. The spectra of these fractions, including the spectrum of a sample of pure dipentene, are shown in figures 3 and 4. In these figures the abscissas are mass numbers, and the ordinates are on a scale of 100 for the maximum peak. Mass spectra like these could serve as a basis for the identification of polymers.

The authors express their indebtedness to F. L. Mohler for many helpful suggestions, to L. Wall for the preparation of some of the polymers, to R. M. Reese and E. Quinn, respectively, for the operation of the mass spectrometer and analysis of the mass spectra, and to M. Tryon, who purified some of the polymers used in this work.

[6] Curves for the polymers studied previously are shown in figure 2 of [2]. However, because of an error, all the temperatures are reported 25 deg C too high. This error has been corrected in figures 1 and 2 of the present work.

7. References

[1] S. L. Madorsky and S. Straus, J. Research NBS **40,** 417 (1948) RP1886; Ind. Eng. Chem. **40,** 484 (1948).
[2] S. L. Madorsky, S. Straus, D. Thompson, and L. Williamson, J. Research NBS **42,** 499 (1949) RP1989; J. Polymer Sci. **4,** 639 (1949).
[3] R. Simha, L. A. Wall, and P. J. Blatz, J. Polymer Sci. **5,** 615 (1950).
[4] R. Simha and L. A. Wall, J. Phys. Chem. **56,** 707 (1952).
[5] Leo A. Wall, J. Research NBS **41,** 315 (1948).
[6] H. H. G. Jellinek, J. Polymer Sci. **4,** 13 (1949).
[7] N. Grassie and H. W. Melville, Proc. Royal Soc. (London) **199,** 1 (1949).
[8] R. L. Shriner and R. C. Fuson, Identification of organic compounds (John Wiley & Sons, Inc., New York, N. Y., 1940).
[9] G. Gee, Trans. Faraday Soc. **36,** 1162 (1940).
[10] D. J. Brawley and S. G. Weissberg, unpublished work.
[11] S. L. Madorsky, J. Polymer Sci. (In press). (1953).

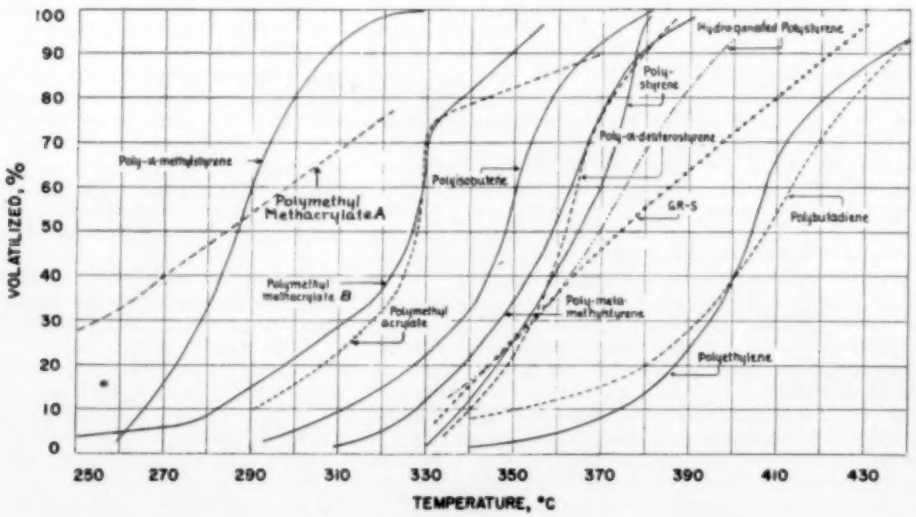


FIGURE 1. *Relative thermal stability of vinyl and diene polymers.*

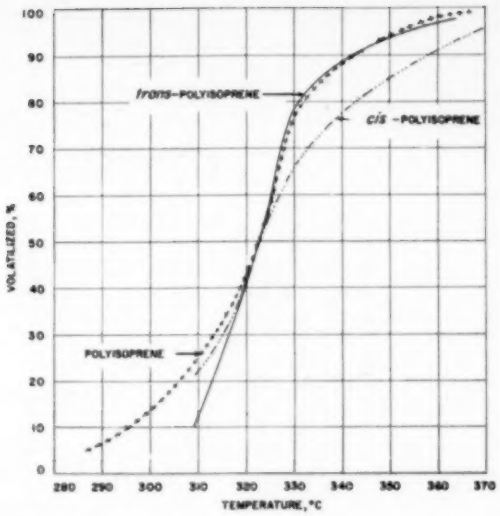


FIGURE 2. *Relative thermal stability of synthetic polyisoprene, natural rubber (cis-polyisoprene), and guttahydrocarbon (trans-polyisoprene).*

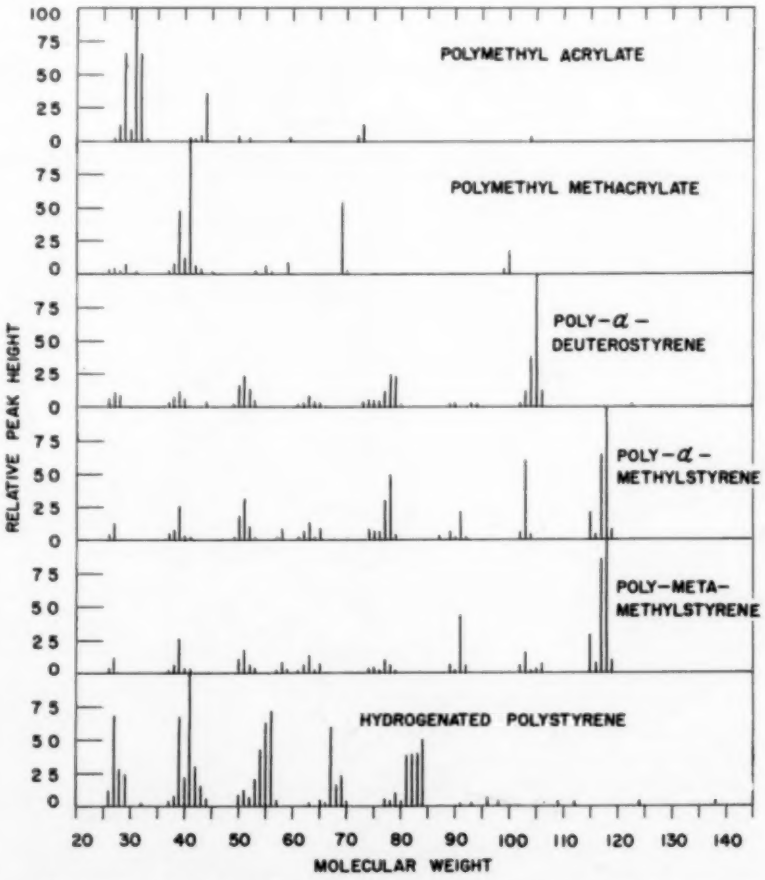


FIGURE 3. *Mass spectra of fraction III obtained in the pyrolysis of polymers.*

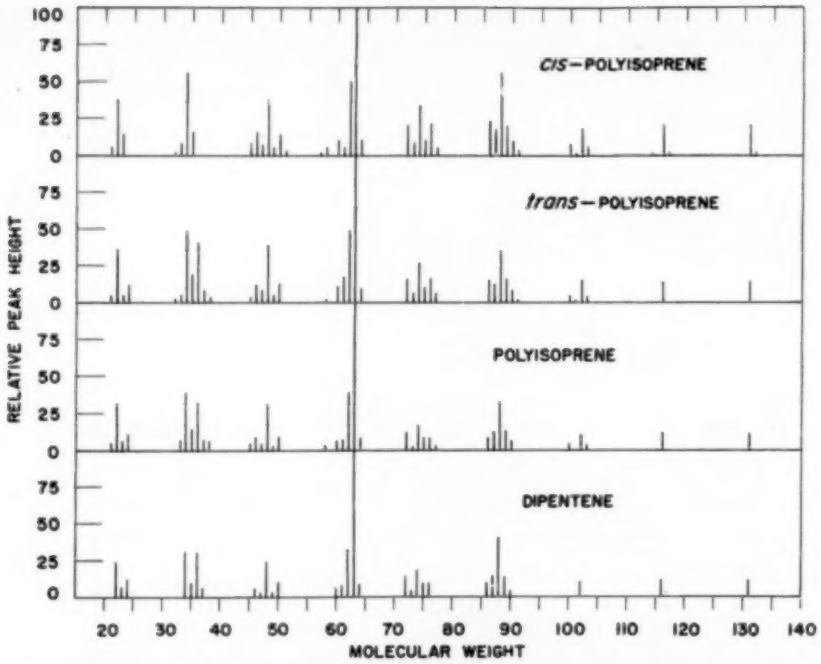


FIGURE 4. *Mass spectra of fraction III obtained in the pyrolysis of synthetic polyisoprene, natural rubber (cis-polyisoprene, guttahydrocarbon (trans-polyisoprene), and dipentene.*

WASHINGTON, June 16, 1952.

Tabulation of an Integral Arising in the Theory of Cooperative Phenomena

Michael Tikson[1]

Integrals of the form

$$\int_0^\pi \int_0^\pi \int_0^\pi f(3b-\cos x-\cos y-\cos z)\,dxdydz \quad (1)$$

occur in problems that involve averages over the characteristic values, λ, of the difference equation

$$\Delta^2 \gamma_{l,m,n}=\lambda\gamma_{l,m,n}, \quad (2)$$

(where Δ^2 is the Laplacian second difference operator) with periodic boundary conditions

$$\gamma_{l,m,n}=\gamma_{l+N,m,n};\quad \gamma_{l,m,n}=\gamma_{l,m+N,n};\quad \gamma_{l,m,n}=\gamma_{l,m,n+N}. \quad (3)$$

Such averages arise in the theory of ferromagnetism, cooperative phenomena in solids, and critical fluctuations in liquids.

In this paper, we deal with the tabulation of

$$I(b)=\frac{1}{\pi^3}\int_0^\pi \int_0^\pi \int_0^\pi \frac{dxdydz}{3b-(\cos x+\cos y+\cos z)} \quad (4)$$

[1][2] for $b^{-1}=\mu=.01(.01)1$.

To obtain $I(b)$ for values of μ from .01 to .8, we represent (4) as a power series in μ by the use of the following relations [1]:

$$\int_0^\pi \int_0^\pi \int_0^\pi (\cos x+\cos y+\cos z)^n dxdydz$$

$$=\left[\frac{\partial^n}{\partial a^n}\int_0^\pi \int_0^\pi \int_0^\pi e^{a(\cos x+\cos y+\cos z)}dxdydz\right]_{a=0} \quad (5)$$

$$=\left[\frac{\partial^n}{\partial a^n}\left\{\int_0^\pi e^{a\cos w}dw\right\}^3\right]_{a=0}=\pi^3\left[\frac{\partial^n}{\partial a^n}\left\{I_0(a)\right\}^3\right]_{a=0}$$

where $I_0(a)$ is the Bessel function of order zero for imaginary argument, which is given by the series

$$I_0(a)=\sum_{k=0}^{\infty}\frac{\left(\frac{a}{2}\right)^{2k}}{(k!)^2}. \quad (6)$$

We obtain

$$I(b)=\frac{\mu}{3}\sum_{k=0}^{\infty}\left(\frac{1}{3}\right)^{2m}(2m)!c_{2m}\mu^{2m} \quad (7)$$

where the c_{2m} are defined by

$$[I_0(x)]^3=\sum_0^\infty c_{2m}x^{2m}; \quad (8)$$

a tabulation of c_{2m} $(m=0, 1, \ldots, 20)$ is given in table 1.

TABLE 1.[a] *Coefficients of* $[I_0(x)]^3=\sum_0^\infty c_{2m}x^{2m}$

Numbers in parentheses stand for the number of zeros between the decimal point and the first significant figure.

$2m$	c_{2m}
0	1.
2	.75
4	.23437 5
6	.04036 4583
8	.00433 34960 9375
10	.00031 55517 57812 5
12	.(4)16562 85038 70081 02
14	.(6)65556 99977 74500 42
16	.(7)20252 65474 70871 28
18	.(9)50173 89455 55226 63
20	.(10)10187 54486 63855 90
22	.(12)17259 66354 77837 00
24	.(14)24766 51388 74193 16
26	.(16)30484 43411 27630 85
28	.(18)32538 95366 70253 00
30	.(20)30405 14661 05592 65
32	.(22)25078 69824 60377 59
34	.(24)18393 02011 96660 07
36	.(26)12073 02467 25867 06
38	.(29)71338 33750 38164 30
40	.(31)38146 15500 21396 56

[a] Although the number of significant figures given here is many more than was required in the calculations for table 2, there may be some general interest in having these coefficients of $[I_0(x)]^3$ available to many places.

At most the first 21 terms of (7) were used to obtain 80 values of $I(b)$ correct to five decimal places. The convergence of (7) is too slow to be used as a practical means of obtaining values of $I(b)$ beyond $\mu=.8$.

The remaining values of $I(b)$ given in the table 2 were obtained by numerical integration. Since the integrand of (4) is infinite for $x=y=z=0$ and $b=1$,

[1] Computation Research Section, Flight Research Laboratory, Wright Air Development Center, USAF. The present computation was performed with the assistance of various members of the Computation Laboratory of the National Bureau of Standards, where the author was a guest worker.

[2] Figures in brackets indicate the literature references at the end of this paper.

TABLE 2. $I(b)$

$\mu=b^{-1}$	$I(b)$	$\mu=b^{-1}$	$I(b)$
.01	0.00333	.51	0.17831
.02	.00667	.52	.18219
.03	.01000	.53	.18610
.04	.01334	.54	.19003
.05	.01667	.55	.19400
.06	.02001	.56	.19799
.07	.02335	.57	.20202
.08	.02670	.58	.20607
.09	.03004	.59	.21017
.10	.03339	.60	.21429
.11	.03674	.61	.21846
.12	.04010	.62	.22266
.13	.04346	.63	.22691
.14	.04682	.64	.23120
.15	.05019	.65	.23553
.16	.05356	.66	.23991
.17	.05694	.67	.24434
.18	.06033	.68	.24882
.19	.06372	.69	.25335
.20	.06712	.70	.25794
.21	.07052	.71	.26259
.22	.07394	.72	.26730
.23	.07736	.73	.27208
.24	.08079	.74	.27694
.25	.08422	.75	.28186
.26	.08767	.76	.28687
.27	.09113	.77	.29196
.28	.09459	.78	.29714
.29	.09807	.79	.30242
.30	.10156	.80	.30781
.31	.10506	.81	.31332
.32	.10857	.82	.31894
.33	.11209	.83	.32469
.34	.11563	.84	.33057
.35	.11918	.85	.33662
.36	.12274	.86	.34284
.37	.12632	.87	.34925
.38	.12992	.88	.35589
.39	.13352	.89	.36277
.40	.13715	.90	.36993
.41	.14079	.91	.37741
.42	.14445	.92	.38526
.43	.14813	.93	.39355
.44	.15183	.94	.40238
.45	.15555	.95	.41189
.46	.15929	.96	.42229
.47	.16304	.97	.43395
.48	.16683	.98	.44758
.49	.17063	.99	.46503
.50	.17446	1.00	.50546

some modification was necessary before numerical integration could be applied. We make use of (4) in the form:

$$I(b)=\frac{1}{\pi^2}\int_0^{\pi}\frac{2}{3b-\cos x}K\left(\frac{2}{3b-\cos x}\right)dx, \quad (9)$$

where K is the complete elliptic integral of the first kind defined by

$$K(u)=\int_0^{\frac{\pi}{2}}\frac{d\theta}{\sqrt{1-u^2\sin^2\theta}}. \quad (10)$$

In carrying out the integration, the integrand in (9) was expressed as the sum of two parts. The first part was the integrand diminished by an expression that removed the singularity and made the numerical integration feasible. This expression was so chosen that it could be integrated in closed form.

As an alternative to the foregoing method, the following procedure was employed as a check on some of the results. If we substitute the series expansion for $K(u)$ in (9) and invert the order of summation and integration, we obtain ultimately

$$I(b)=(9b^2-1)^{-\frac{1}{2}}+\sum_{n=1}^{\infty}\left[\frac{1\cdot3\cdot5\cdots(2n-1)}{2\cdot4\cdot6\cdots(2n)}\right]^2\frac{2^{2n}g_{2n}}{(2n)!}, \quad (11)$$

where $g_n=[d^n/d^n(3b)]\{[9b^2-1]^{-\frac{1}{2}}\}$. We note that g_n satisfies the following recurrence relation

$$(9b^2-1)g_{n+1}+3b(2n+1)g_n+n^2g_{n-1}=0. \quad (12)$$

[1] E. W. Montroll, Nuovo Cimento, [9] **6**, 265 (1941).
[2] G. N. Watson, Quart. J. Mathematics **10**, 266 (Oxford 1939).
[3] E. Jahnke and F. Emde, Funktionentafeln mit Formeln und Kurven, 2d *ed*, p. 145 (1909).
[4] H. B. Dwight, Tables of integrals and other mathematical data, p. 123 (Macmillan Co., New York, N. Y., 1947).
[5] T.H. Berlin and M. Kac, The spherical model of a ferromagnet, Johns Hopkins University, ONR Report N60 NR-293, Task Order 18, and N60 NR-246, Task Order 5.

WASHINGTON, November 26, 1952.